MAP: STRUCTURE AND PROPERTIES (TRO)



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Map: Structure and Properties (Tro)

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Licensing

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CHAPTER OVERVIEW

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1.1: A Particulate View of the World - Structure Determines Properties

Matter is anything that occupies space and has mass. Matter has bulk properties that we can directly observe and investigate. For example, why is water a liquid at room temperature and at atmospheric pressure? What makes a drug effective or toxic? Why is steel a strong solid and not a liquid like mercury? Why can we ignite a hdryogen gas, but not helium (Figure 1.1.1)?



Figure 1.1.1: (left) The hydrogen gas used in the *Hindenburg* Zepplin is a highly flammable gas (Public Domain; Sam Shere via Wikipedia). (right) In contrast, the helium used in the Goodyear blimp is nonflammable and considerably safer. (CC BY-SA 3.0; Hughs via Wikipedia)

To address these questions, we must first understand two fundamentals concepts of matter that underlie all of chemistry.

1. All matter is consist of small particles, which is the basis of modern atomic theory, and
2. The structure of these particles determines the properties that the matter.

A common refrain taught in biology classes is that **Structure Determines Function**. The chemistry-centered reformulation of this concept is that **Structure Determines Properties**, which is a useful theme in chemistry and in fields that chemistry plays an important role including biology, environmental science, biochemistry, polymer science, medicine, engineering, and nutrition among many others. However, what is meant by properties and structure?

Properties are generally separated into either chemical properties (e.g., will a reaction happen and under what conditions will it occur) or physical properties (e.g., what is a substance' melting points, boiling points, solubility). But what we we mean about structure? This is a catch all phrase for the size, geometry and nature of the atoms of the particulates that the matter is composed of. As you progress through the topics of this chemistry text, we will remind you of this central concept and its applications.

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1.2: Classifying Matter- A Particulate View

Learning Objectives

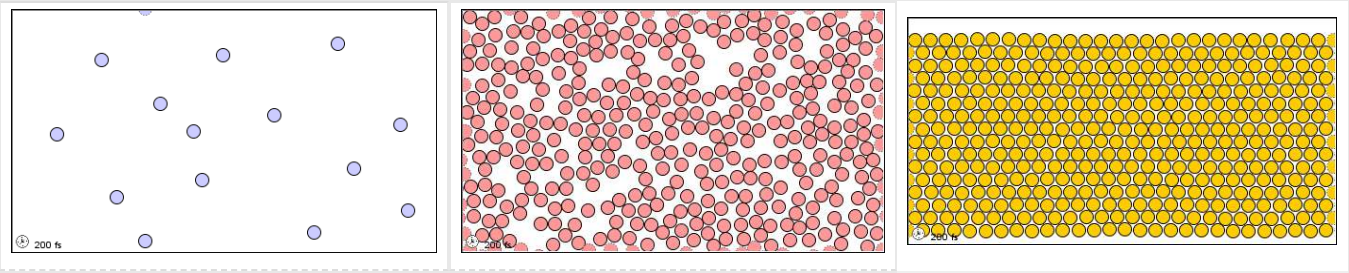
- To classify matter into the three primary states of matter
- Separate homogeneous from inhomogeneous mixtures

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



Figure 1.2.1: The three common states of matter. From the left, they are solid, liquid, and gas, represented by an ice sculpture, a drop of water, and the air around clouds, respectively. Images used with permission from Wikipedia.

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces are attractive forces that try to draw the particles together (Figure 1.2.2). Gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.



gaseous state	*liquid*	*solid*

Figure 1.2.2: 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.

Elements, Compounds, 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.

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.

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!)

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

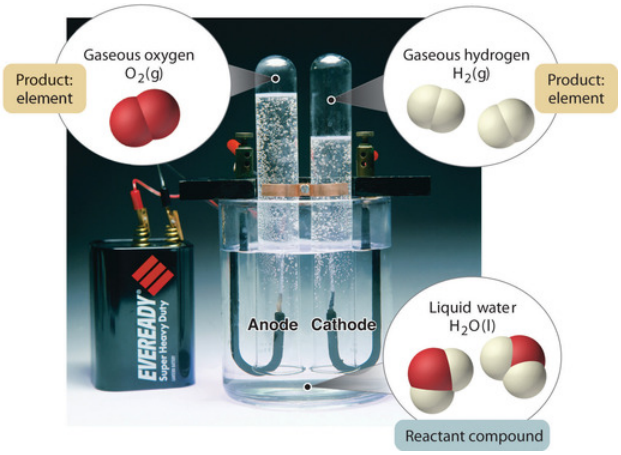


Figure 1.2.3: The Decomposition of Water to Hydrogen and Oxygen by Electrolysis. Water is a chemical compound; hydrogen and oxygen are elements.

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 called electrolysis. In electrolysis, electricity provides the energy needed to separate a compound into its constituent elements (Figure 1.2.3). A similar technique is used on a vast scale to obtain pure aluminum, an element, from its ores, which are mixtures of compounds. Because a great deal of energy is required for electrolysis, the cost of electricity is by far the greatest expense incurred in manufacturing pure aluminum. Thus recycling aluminum is both cost-effective and ecologically sound.

The overall organization of matter and the methods used to separate mixtures are summarized in Figure 1.2.4.

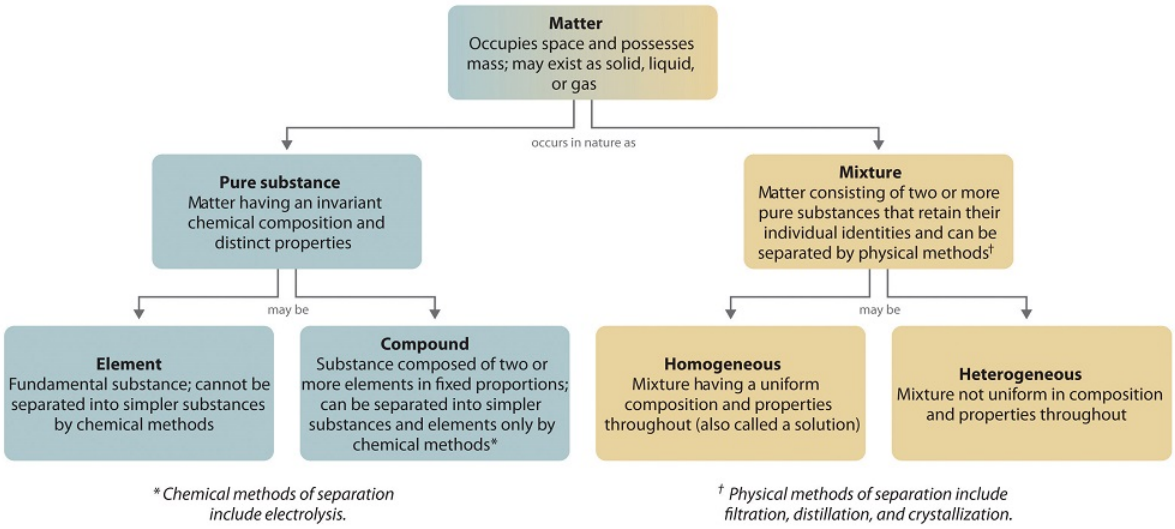


Figure 1.2.4: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Example 1.2.1

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

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

Given: a chemical substance

Asked for: its classification

Strategy:

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

Solution

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

? Exercise 1.2.1

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

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

Answer A

solution

Answer B

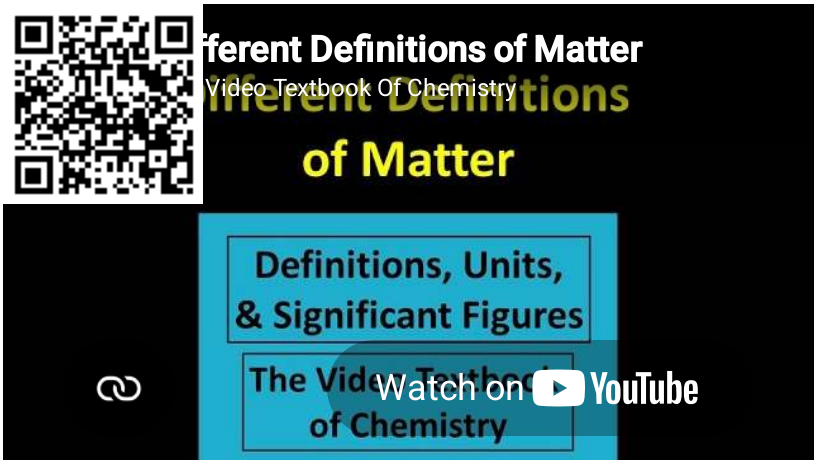
element

Answer C

heterogeneous mixture

Answer D

compound



Different Definitions of Matter: https://youtu.be/qi_qLHc8wLk

Summary

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.

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1.3: The Scientific Approach to Knowledge

Learning Objectives

- Give a short history of the concept of the atom.
- Describe the contributions of Democritus and Dalton to atomic theory.
- Summarize Dalton's atomic theory and explain its historical development.

We discussed the particulate model of matter, but this is not a clear conclusion to the casual observer of nature. While all modern scientists accept the concept of the atom, when the concept of the atom was first proposed about 2,500 years ago, ancient philosophers laughed at the idea. It has always been difficult to convince people of the existence of things that are too small to see. We will spend some time considering the evidence (observations) that convince scientists of the existence of atoms.

About 2,500 years ago, early Greek philosophers believed the entire universe was a single, huge, entity. In other words, "everything was one." They believed that all objects, all matter, and all substances were connected as a single, big, unchangeable "thing." One of the first people to propose "atoms" was a man known as Democritus. As an alternative to the beliefs of the Greek philosophers, he suggested that **atomos**, or atomon - tiny, indivisible, solid objects - make up all matter in the universe.



Figure 1.3.1: (left) Democritus by Hendrick ter Brugghen, 1628. Democritus was known as the "laughing philosopher." It was a good thing he liked to laugh, because most other philosophers were laughing at his theories. (right) British physicist and chemist John Dalton (1766-1844). Unlike the Greek philosophers, John Dalton believed in both logical thinking and experimentation.

Democritus then reasoned that changes occur when the many atomos in an object were reconnected or recombined in different ways. Democritus even extended this theory, suggesting that there were different varieties of atomos with different shapes, sizes, and masses. He thought, however, that shape, size, and mass were the only properties differentiating the different types of atomos. According to Democritus, other characteristics, like color and taste, did not reflect properties of the atomos themselves, but rather, resulted from the different ways in which the atomos were combined and connected to one another.

The early Greek philosophers tried to understand the nature of the world through reason and logic, but not through experiment and observation. As a result, they had some very interesting ideas, but they felt no need to justify their ideas based on life experiences. In a lot of ways, you can think of the Greek philosophers as being "all thought and no action." It's truly amazing how much they achieved using their minds, but because they never performed any experiments, they missed or rejected a lot of discoveries that they could have made otherwise. Greek philosophers dismissed Democritus' theory entirely. Sadly, it took over two millennia before the theory of atomos (or "atoms," as they're known today) was fully appreciated.

Greeks: "All thought and No Action"

Greek philosophers were "all thought and no action" and did not feel the need to test their theories with reality. In contrast, Dalton's efforts were based on experimentation and testing ideas against reality.

While it must be assumed that many more scientists, philosophers, and others studied composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800's with the work of the British scientists John Dalton. His **atomic theory** is a fundamental concept that states that all elements are composed of atoms. Dalton formulated his theory by focusing on experimental results (in contrast to the ancient Greek philosophers) by studied the weights of

various elements and compounds. From his experiments and observations, as well as the work from peers of his time, Dalton proposed a new theory of the **atom**.The general tenets of this theory were as follows:

- All matter is composed of extremely small particles called atoms.
- Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
- Atoms cannot be subdivided, created, or destroyed.
- Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
- In chemical reactions, atoms are combined, separated, or rearranged.

Dalton's atomic theory has been largely accepted by the scientific community, with the exception of three changes. We know now that (1) an atom can be further subdivided, (2) all atoms of an element are not identical in mass, and (3) using nuclear fission and fusion techniques, we can create or destroy atoms by changing them into other atoms.

The evidence for atoms is so great that few doubt their existence. In fact, individual atoms are now routinely observed with state-of-the art technologies.

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 1.3.2).

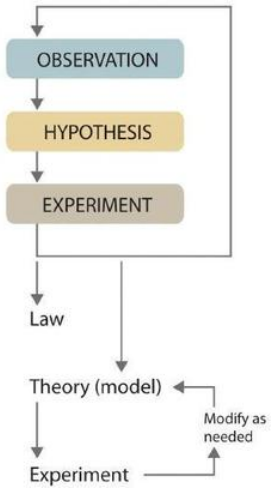
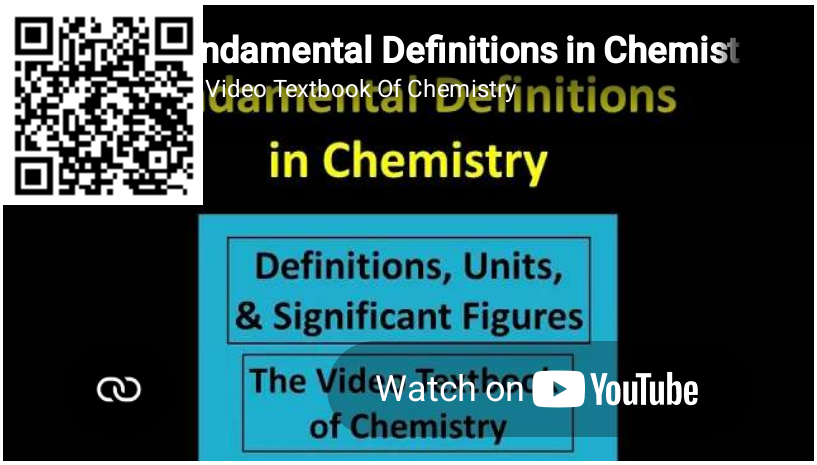


Figure 1.3.2: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

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 acid forms a blue solution and a brown gas. 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. 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 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.

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.



Fundamental Definitions in Chemistry: https://youtu.be/SBwjbkFNkdw

Measurementsunderlie the Scientific Method

The results of a scientific experiment must be communicated to be of value. This affords an opportunity for other scientists to check them. It also allows the scientific community, and sometimes the general public, to share new knowledge. Communication, however, is not always as straightforward as it might seem. Ambiguous terminology can often turn a seemingly clear statement into a morass of misunderstanding.

As an example, consider someone tells you that the forecast is a high of 25°. Do you put on a winter jacket, or summer wear? If you are thinking winter, then you interpreted the temperature as 25°F. However if 25°C was meant, which is equal to 77°F, a winter jacket would be far too warm. Or consider filling up a car with gasoline. If you are in the US, you will be dealing in dollars per gallon, whereas, if you were in continental Europe, you will be dealing in Euros per liter. Given that the exchange rate from USD to Euros fluctuates and that there are roughly 3.79 liters in 1 gallon, it is difficult to simply compare numbers between gas prices in the USA, and say, France, if you don't know what units you are using. As a final example, consider the speed 24 meters/sec. Do you interpret this as close to highway speed limits in the US? It is the same speed as 53.7 miles per hour, likely a more familiar set of units for speed for people in the US.

Scientists are not all that different from other people—they too have favorite units which are especially suited to certain areas of research. Nevertheless, scientists have constantly pressed for improvement and uniformity in systems of measurement. The first such action occurred nearly 200 years ago when, in the aftermath of the French Revolution, the *metric system* spread over most of continental Europe and was adopted by scientists everywhere. The United States nearly followed suit, but in 1799 Thomas Jefferson was unsuccessful in persuading Congress that a system based on powers of 10 was far more convenient and would eventually become the standard of the world.

The metric system has undergone continuous evolution and improvement since its original adoption by France. Beginning in 1899, a series of international conferences have been held for the purpose of redefining and regularizing the system of units. In 1960 the Eleventh Conference on Weights and Measures proposed major changes in the metric system and suggested a new name — the **International System of Units** — for the revised metric system. (The abbreviation **SI**, from the French *Système International*, is commonly used.) Scientific bodies such as the U.S. National Bureau of Standards and the International Union of Pure and Applied Chemistry have endorsed the SI.

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.
- 2,500 years ago, Democritus suggested that all matter in the universe was made up of tiny, indivisible, solid objects he called "atomos." However, other Greek philosophers disliked Democritus' "atomos" theory because they felt it was illogical. Dalton's Atomic Theory is the first scientific theory to relate chemical changes to the structure, properties, and behavior of the atom.
- 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.

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1.4: Early Ideas about the Building Blocks of Matter

The ancient Greek philosophers did a lot of discussing, with part of their conversations concerning the physical world and its composition. There were different opinions about what made up matter. Some felt one thing was true while others believed another set of ideas. Since these scholars did not have laboratories and had not developed the idea of the experiment, they were left to debate. Whoever could offer the best argument was considered right. However, often the best argument had little to do with reality. One of their ongoing debates had to do with sand. The question posed was: into how small of pieces can you divide a grain of sand? The prevailing thought at the time, pushed by Aristotle, was that the grain of sand could be divided indefinitely, that you could always get a smaller particle by dividing a larger one and there was no limit to how small the resulting particle could be.

Since Aristotle was such an influential philosopher, very few people disagreed with him. However, there were some philosophers who believed that there was a limit to how small a grain of sand could be divided. One of these philosophers was Democritus (~460 - ~370 B.C.E.), often referred to as the "laughing philosopher" because of his emphasis on cheerfulness (Figure 1.4.1). He suggested that **atomos**, or atomon - tiny, indivisible, solid objects - make up all matter in the universe.



Figure 1.4.1: (left) Democritus by Hendrick ter Brugghen, 1628. Democritus was known as the "laughing philosopher." It was a good thing he liked to laugh, because most other philosophers were laughing at his theories. (right): British physicist and chemist John Dalton (1766-1844). Unlike the Greek philosophers, John Dalton believed in both logical thinking and experimentation.

Democritus then reasoned that changes occur when the many atomos in an object were reconnected or recombined in different ways. Democritus even extended this theory, suggesting that there were different varieties of atomos with different shapes, sizes, and masses. He thought, however, that shape, size, and mass were the only properties differentiating the different types of atomos. According to Democritus, other characteristics, like color and taste, did not reflect properties of the atomos themselves, but rather, resulted from the different ways in which the atomos were combined and connected to one another.

Aristotle disagreed with Democritus and offered his own idea of the composition of matter. According to Aristotle, everything was composed of four elements: earth, air, fire, and water. The theory of Democritus explained things better, but Aristotle was more influential, so his ideas prevailed. We had to wait almost two thousand years before scientists came around to seeing the atom as Democritus did.

It is very interesting that Democritus had the basic idea of atoms, even though the had no experimental evidence to support his thinking. We now know more about how atoms hold together in "clusters" (compounds), but the basic concept existed over two thousand years ago. We also know that atoms can be further subdivided, but there is still a lower limit to how small we can break up that grain of sand.

Greeks Philosophers were not Scientists

Greek philosophers were "all thought and no action" and did not feel the need to test their theories with reality via experiments and the scientific method. Dalton's atomic theory were based on experimentation and testing ideas against reality.

Summary

The early Greek philosophers tried to understand the nature of the world through reason and logic, but not through experiment and observation. As a result, they had some very interesting ideas, but they felt no need to justify their ideas based on life experiences. In a lot of ways, you can think of the Greek philosophers as being "all thought and no action." It's truly amazing how much they

achieved using their minds, but because they never performed any experiments, they missed or rejected a lot of discoveries that they could have made otherwise. Greek philosophers dismissed Democritus' theory entirely. Sadly, it took over two millennia before the theory of atomos (or "atoms," as they're known today) was fully appreciated.

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1.5: Modern Atomic Theory and the Laws That Led to It

Learning Objectives

- Correctly define a law as it pertains to science.
- Understand the application of the application of the law of conservation of matter.
- Understand the application of the law of definite proportions
- Understand the application of the law of multiple proportions
- Understand the basis of Dalton's Atomic Theory

With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist A. Lavoisier laid the foundation to the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. While John Dalton is credited for proposing modern atomic theory. Dalton built his theory upon laws previously identified by Lavoisier and Proust as a basis for his atomic theory:

1. Law of Conservation of Mass,
2. Law of Definite Proportions, and
3. Law of Multiple Proportions.

Law of 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. This law, which is central is the **law of conservation of matter** (also known as the "law of indestructibility of matter") and states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is *conserved*. According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

> *Law of Conservation Conservation of Mass states that in a chemical reaction, matter is neither created nor destroyed.*



Figure 1.5.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before (Figure 1.5.1). When wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose we had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose we had been able to measure the oxygen used by the fire and the gases produced by the fire. What would we find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

Example 1.5.1

If heating 10 grams of $CaCO_3$ produces 4.4 g of CO_2 and 5.6 g of CaO, show that these observations are in agreement with the law of conservation of mass.



Figure 1.5.1: A sample of calcium carbonate ($CaCO_3$). (Public Domain; Walkerma).

Solution

- Mass of the reactants, $CaCO_3$: $10\,g$
- Mass of the products, CO_2 and CaO: $4.4\,g + 5.6\,g = 10\,g$.

Because the mass of the reactants = the mass of the products, the observations are in agreement with the law of conservation of mass.

Exercise 1.5.1

a. What is the law of conservation of matter?
b. How does the law of conservation of matter apply to chemistry?

Answer a

The law of conservation of matter states that in any given system that is closed to the transfer of matter, the amount of matter in the system stays constant

Answer b

The law of conservation of matter says that in chemical reactions, the total mass of the products must equal the total mass of the reactants.

The Law of Definite Proportions

Joseph Proust (1754-1826) formulated the **law of definite proportions** (also called the Law of Constant Composition or Proust's Law), which 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. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 1.5.1.

Table 1.5.1: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82\text{ g carbon}}{2.78\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$
B	22.33 g	4.19 g	$\frac{22.33\text{ g carbon}}{4.19\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$
C	19.40 g	3.64 g	$\frac{19.40\text{ g carbon}}{3.63\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds

other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

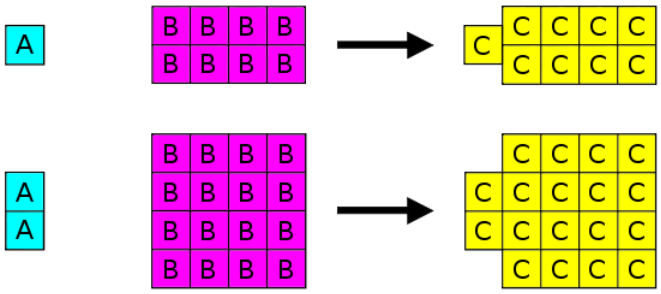


Figure 1.5.2: If 1 gram of A reacts with 8 grams of B, then by the Law of Definite Proportions, 2 grams of A must react with 16 grams of B. If 1 gram of A reacts with 8 grams of B, then by the Law of Conservation of Mass, they must produce 9 grams of C. Similarly, when 2 grams of A react with 16 grams of B, they must produce 18 grams of C.

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

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

Example 1.5.2: 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.

The Law of Multiple Proportions

The **law of multiple proportions** (sometime call Dalton's Law) states that if two elements form more than one compound between them, then the ratios of the masses of the second element which combine with a fixed mass of the first element will always be ratios of small whole numbers. 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.

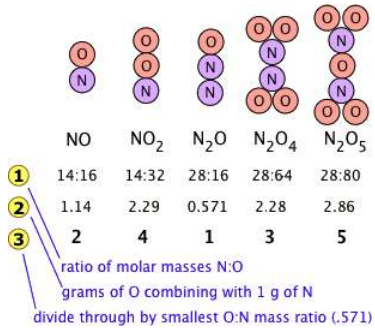


Figure 1.5.3: Law of Multiple Proportions applied to nitrogen oxides (NO_x) compounds. (CC-BY; Stephen Lower)

- Line ① shows the ratio of the relative weights of the two elements in each compound. These ratios were calculated by simply taking the molar mass of each element, and multiplying by the number of atoms of that element per mole of the compound.

Thus for NO_2, we have (1 × 14) : (2 × 16) = 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 1.5.3: Oxides of Carbon

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

Solution

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

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

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

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

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

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

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

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

John Dalton and the Atomic Theory

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 1.5.4), 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).

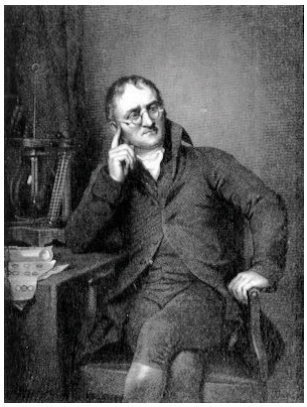


Figure 1.5.4: John Dalton was an English scientist who enunciated the modern atomic theory.

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.

Deficiencies of Dalton's Theory

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.

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

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Summary

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

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1.6: The Discovery of the Electron

Learning Objectives

- To become familiar with the feature of an electron.
- Summarize and interpret the results of the experiments of Thomson and Millikan.

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 1.6.1). 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". 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.

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.

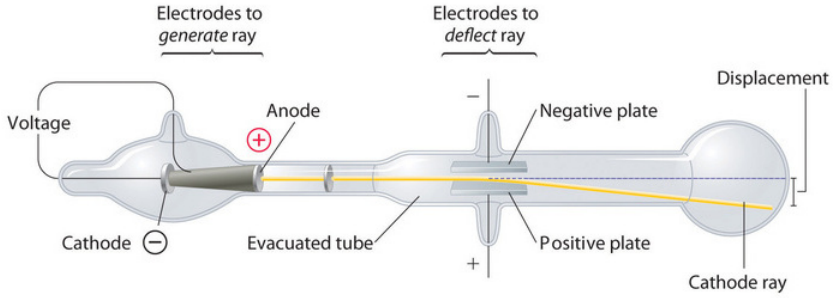


Figure 1.6.1: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged. (CC BY-SA-NC 3.0; anonymous)

Aside: Electrostatic Forces

If two objects each have electric charge, then they exert an exert an electric force on each other. The magnitude of the force is linearly proportional the charge on each object and inversely proportional to square distance between each other. The magnitude of this **electrostatic force** is linearly proportional the distance between them and involves the existence of two types of charge, the observation that like charges repel, unlike charges attract and the decrease of force with distance.

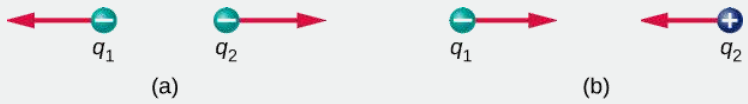


Figure 1.6.2: The electrostatic force between point charges q_1 and q_2 separated by a distance. (a) If the charges have the same sign, the force is in the same direction as showing a repelling force. (b) If the charges have different signs, the force is in the opposite direction showing an attracting force. (CC BY 4.0; OpenStax (modified))

The SI unit of electric charge is the coulomb (C) named after French physicist Charles-Augustin de Coulomb.

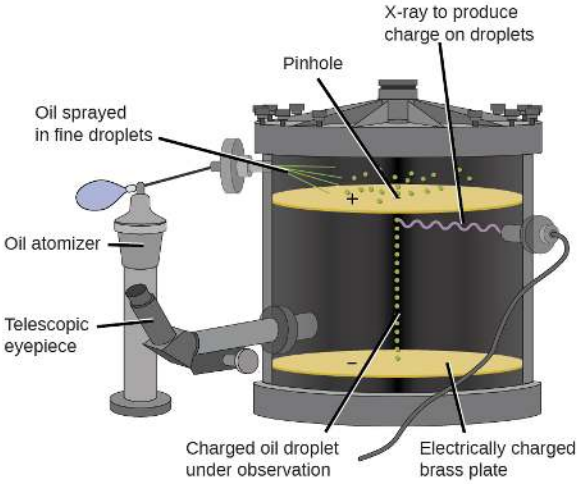
The video below shows JJ Thompson used such tube to measure the ratio of charge over mass of an electron.



Video 1.6.1: Measuring e/m For an Electron. Video from Davidson College demonstrating Thompson's e/m experiment.

Millikan's Oil Drop Experiment: Measuring the Charge of the Electron

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. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 1.6.2).



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure 1.6.3: Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values. (CC BY 4.0; OpenStax).

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, $1.6 \times 10^{-19}\ C$. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron ($1 \times (1.6 \times 10^{-19}\ C)$), two electrons ($2 \times (1.6 \times 10^{-19}\ C)$), three electrons ($3 \times (1.6 \times 10^{-19}\ C)$), and so on, on a given oil droplet.

Defintion: Elementary Charge

The charge of an electron is sometimes referred to as the **elementary charge** and usually denoted by e. The elementary charge is a fundamental physical constant and as of May 2019, its value is *defined* to be exactly $1.602176634 \times 10^{-19}\ C$.

Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research ($1.759 \times 10^{11}\ C/kg$), it only required a simple calculation to determine the mass of the electron as well.

$$\text{Mass of electron} = 1.602 \times 10^{-19} \cancel{C} \times \frac{1\ \text{kg}}{1.759 \times 10^{11} \cancel{C}}$$

$$= 9.107 \times 10^{-31}\ \text{kg}$$

Scientists had now established that the atom was not indivisible as Dalton's theory had postulated, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood.

? Exercise 1.6.1

In a Millikan's oil drop experiment done in alternate universe, the measured charges on drops are found to be $8 \times 10^{-19}\ C$, $12 \times 10^{-19}\ C$ and $20 \times 10^{-19}\ C$. What is the elementary charge in this universe?

Answer

Millikan experiment involves confirm that the charges of the drops were all small integer multiples of the elementary charge. The charges on the drop are found to be multiple of 4. Hence the small charge are $4 \times 10^{-19} C$.

Contributors and Attributions

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1.7: The Structure of The Atom

Learning Objectives

- Outline milestones in the discovery of the nucleus
- Summarize and interpret the results of the Rutherford's gold-foil scatter experiments

Thompson's Non-nuclear Model

Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure 1.7.1). A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons.

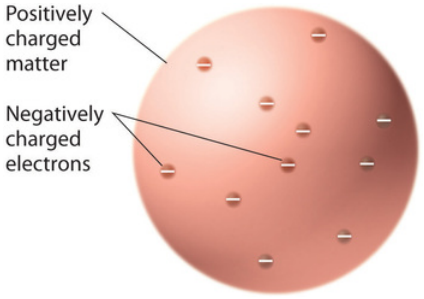


Figure 1.7.1: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge. (CC BY-SA-NC; anonymous).

Rutherford's Nuclear Model

The next major development in understanding the atom came from Ernest Rutherford (1871 to 1937), a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged alpha particles (α particles) that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

This experiment showed unambiguously that Thomson's model of the atom (Figure 1.7.1) was incorrect. Rutherford aimed a stream of α particles at a very thin gold foil target (Figure 1.7.2*a*) and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets, minimizing the number of atoms in the target. If Thomson's model of the atom were correct, the positively-charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (Figure 1.7.2*b*). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (Figure 1.7.2*c*). 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."

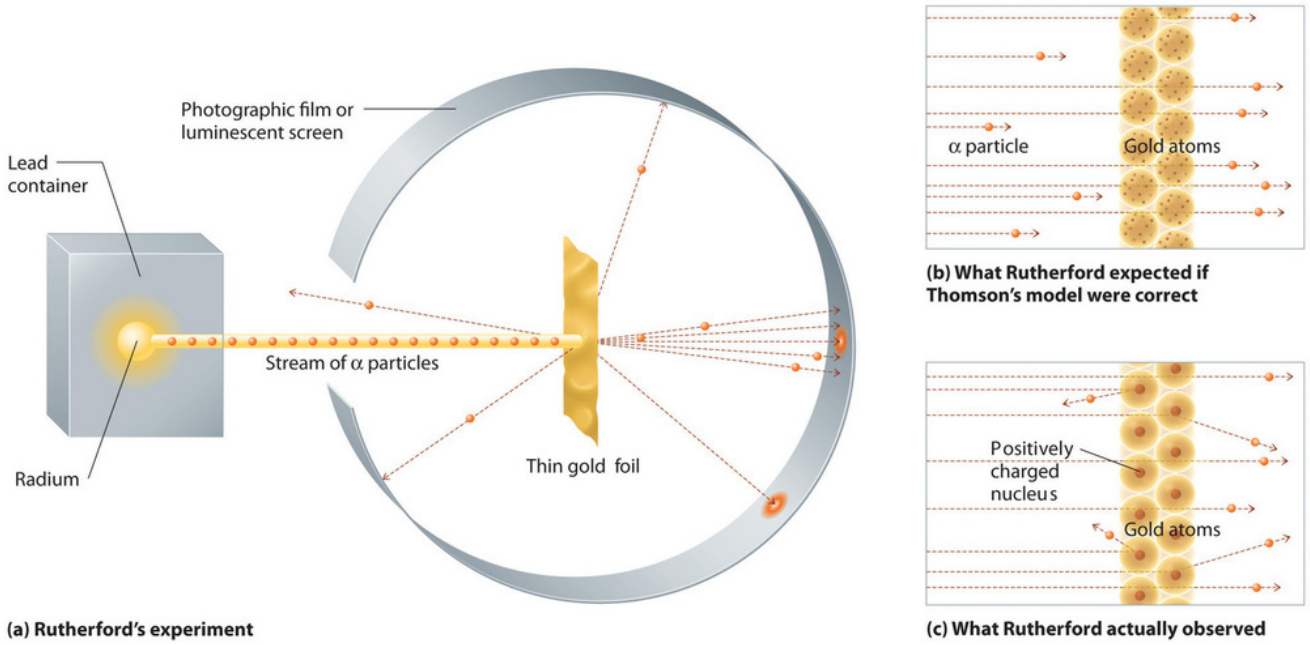


Figure 1.7.2: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles 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. (CC BY-SA-NC; anonymous).

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.

Intranuclear Structure

Rutherford and other scientists decided that a positively charged nuclear consists of 'positive electrons' to balance the charge of the surrounding electrons; this term **proton** was formally assigned to this particle by 1920. However, Rutherford could not explain why repulsions between the protons in the nuclei that contained more than one positive charge did not cause the nucleus to disintegrate, he reasoned that electrostatic 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 nucleus together.

The historical development of the different models of the atom's structure is summarized in Figure 1.7.3. 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.

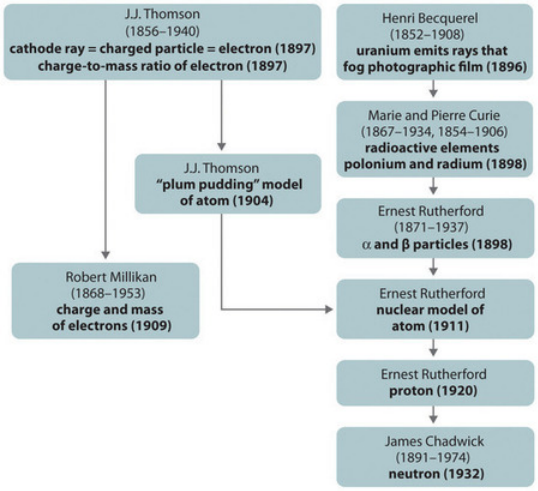


Figure 1.7.3: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed. Image used with Permission (CC BY-SA-NC; anonymous).

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.

Contributors

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1.8: Subatomic Particles - Protons, Neutrons, and Electrons

Learning Objectives

- To know the meaning of isotopes and atomic masses.

To date, about 118 different elements have been discovered; by definition, each is chemically unique. To understand why they are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of its components. Atoms consist of electrons, protons, and neutrons. Although this is an oversimplification that ignores the other subatomic particles that have been discovered, it is sufficient for discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 1.8.1, 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 1.8.1: Properties of Subatomic Particles*

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

Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense) *nucleus* which carries a positive electric charge and almost all of the *volume* of an atom consists of empty space in which electrons reside (Figure 1.8.1). 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.

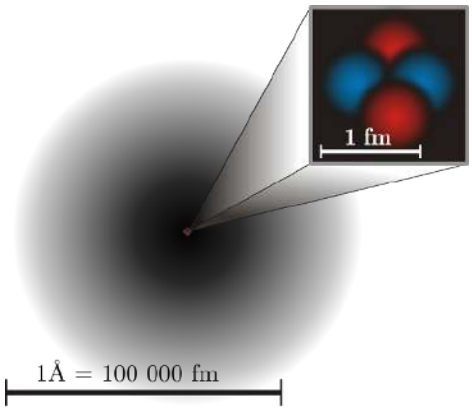


Figure 1.8.1: The structure of helium atom with a central nucleus and surrounding electrons. (CC BY-SA 3.0; Yzmo via Wikipedia)

The Number of Protons Define the Nature of the Elements

The number of protons in the nucleus of an atom is its **atomic number** (Z). This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its mass number (A)). The number of neutrons is therefore the difference between the mass number and the atomic number:

$$\begin{aligned} \text{atomic number (Z)} &= \text{number of protons} \\ \text{mass number (A)} &= \text{number of protons} + \text{number of neutrons} \\ \text{A}-\text{Z} &= \text{number of neutrons} \end{aligned}$$

The identity of an element is defined by Z, the number of protons in the nucleus of an atom of the element, which is different for each element. The known elements are arranged in order of increasing Z in the **periodic table** (Figure 1.8.2). 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.

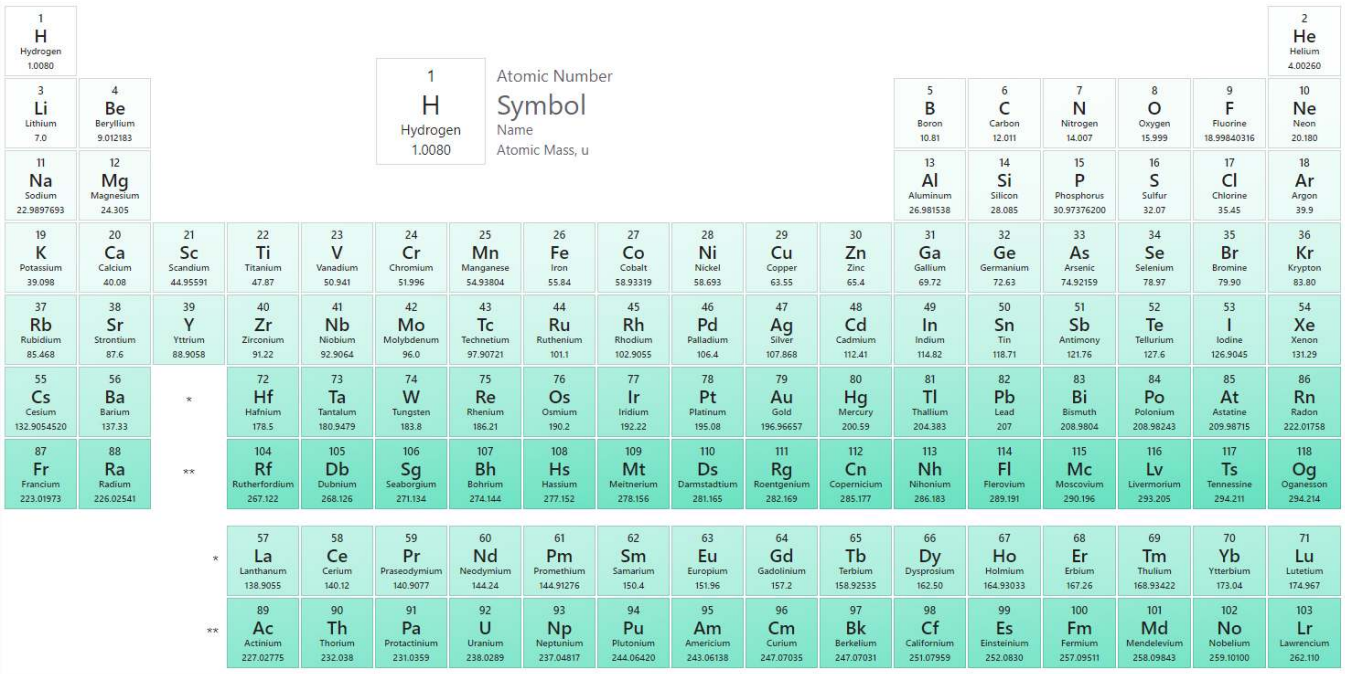


Figure 1.8.2: Periodic Table of Elements that is color coded for atomic mass. Notice the elements at the bottom of the table have a greater mass than elements at the top. (PubChem via National Center for Biotechnology Information (2020).

The symbols for several common elements and their atoms are listed in Table 1.8.2. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

Table 1.8.2: Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists or locations; for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements

Isotopes: Differing Numbers of Neutrons

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

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

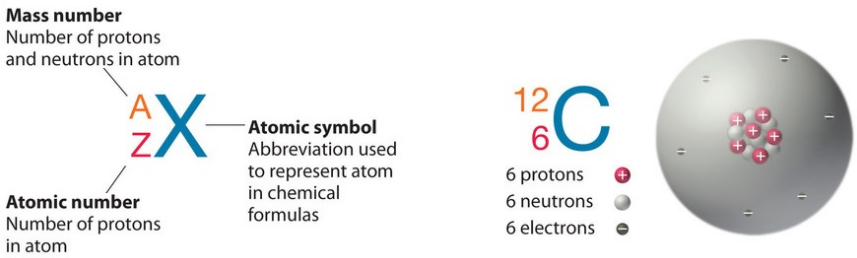


Figure 1.8.3: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript.

For example, naturally occurring hydrogen has two stable nuclides, ${}^{1}_{1}\mathrm{H}$ and ${}^{2}_{1}\mathrm{H}$, which also are isotopes of one another. More than 99.98 percent is "light" hydrogen, ${}^{1}_{1}\mathrm{H}$. This consists of atoms each of which has one proton, one electron, and zero neutrons (Figure 1.8.1;). The rest is "heavy" hydrogen or deuterium, ${}^{2}_{1}\mathrm{H}$, which consists of atoms which contain one electron, one proton, and one neutron (Figure 1.8.1;. Hence the nuclidic mass of deuterium is almost exactly twice as great as for light hydrogen. It is also possible to obtain a third isotope, tritium, ${}^{3}_{1}\mathrm{H}$. that consists of atoms whose nuclei contain two neutrons and one proton (Figure 1.8.1;). Its mass is about 3 times that of light hydrogen.

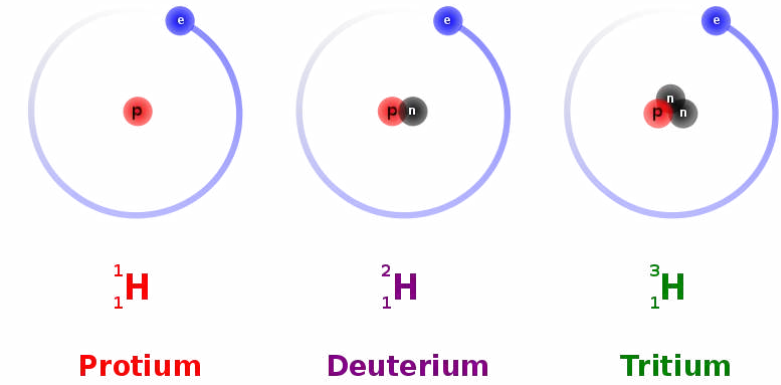


Figure 1.8.4: Above are the three isotopes of Hydrogen. Each have the same number of protons, but have different numbers of neutrons in the nucleus. (CC BY-SA 3.0; Balajijagadesh via Wikipedia)

In addition to ${}^{12}C$, a typical sample of carbon contains 1.11% ${}^{13}_{6}C$ (${}^{13}\mathrm{C}$), with 7 neutrons and 6 protons, and a trace of ${}^{14}_{6}C$ (${}^{14}\mathrm{C}$), with 8 neutrons and 6 protons. The nucleus of ${}^{14}\mathrm{C}$ 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. Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 1.8.2. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ${}^{2}\mathrm{H}$, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ${}^{3}\mathrm{H}$, is also called tritium and sometimes symbolized T.

Table 1.8.3: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}\mathrm{H}$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}\mathrm{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}\mathrm{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}\mathrm{He}$	2	2	1	3.01603	0.00013
	$^{4}_{2}\mathrm{He}$	2	2	2	4.0026	100
lithium	$^{6}_{3}\mathrm{Li}$	3	3	3	6.0151	7.59
	$^{7}_{3}\mathrm{Li}$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}\mathrm{Be}$	4	4	5	9.0122	100
boron	$^{10}_{5}\mathrm{B}$	5	5	5	10.0129	19.9
	$^{11}_{5}\mathrm{B}$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}\mathrm{C}$	6	6	6	12.0000	98.89
	$^{13}_{6}\mathrm{C}$	6	6	7	13.0034	1.11
	$^{14}_{6}\mathrm{C}$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}\mathrm{N}$	7	7	7	14.0031	99.63
	$^{15}_{7}\mathrm{N}$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}\mathrm{O}$	8	8	8	15.9949	99.757
	$^{17}_{8}\mathrm{O}$	8	8	9	16.9991	0.038
	$^{18}_{8}\mathrm{O}$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}\mathrm{F}$	9	9	10	18.9984	100
neon	$^{20}_{10}\mathrm{Ne}$	10	10	10	19.9924	90.48
	$^{21}_{10}\mathrm{Ne}$	10	10	11	20.9938	0.27
	$^{22}_{10}\mathrm{Ne}$	10	10	12	21.9914	9.2

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.

Example 1.8.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland. The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 − 53 = 74). Since the iodine is added as a 1− anion, the number of electrons is 54 [53 – (1–) = 54].

? Exercise 1.8.1

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Answer

78 protons; 117 neutrons; charge is 4+

✔ Example 1.8.2

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 1.8.2

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 ${}^{81}\mathrm{Br}$.

Ions: Charged

The protons and neutrons in the nucleus of an atom are held very tightly by strong nuclear forces. It is very difficult either to separate the nuclear particles or to add extra ones. The electrons, on the other hand, are held to the atom by their electrostatic attraction for the positively charged protons in the nucleus. This force is strong, but not so strong that an atom cannot lose or gain electrons. Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons} \tag{1.8.1}$$

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an anion. Positively charged atoms

called **cations** are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = 1+).

$$\mathrm{Na} + \mathrm{e}^- \longrightarrow \mathrm{Na}^+ \tag{1.8.2}$$

Similarly, a neutral fluorine atom (F = 9) has nine electrons, and if it gains a electron it will become an **anion** with a 1− charge (9 − 10 = 1−).

$$\mathrm{F} - 2\,\mathrm{e}^- \longrightarrow \mathrm{F}^{-2} \tag{1.8.3}$$

The charge of the species has a profound affect on the properties of the species. For example, neutral sodium atoms are unstable and reacting violently when combined with most substnces. However, sodium cations are quite inert; in fact, we eat them all the time as part of sodium chloride (table salt). As we will discussed later, cations and anions almost always occur together to ensure that matter is neutral.

Summary

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

Contributors and Attributions

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1.9: Atomic Mass- The Average Mass of an Element's Atoms

Learning Objectives

- to know the meaning of isotopes and atomic masses.

There are 21 elements with only one isotope, so all their atoms have identical masses. All other elements have two or more isotopes, so their atoms have at least two different masses. However, all elements obey the law of definite proportions when they combine with other elements, so they *behave as if* they had just one kind of atom with a definite mass. To solve this dilemma, we define the **atomic mass** as the weighted average mass of all naturally occurring isotopes of the element.

A atomic mass is defined as

$$\text{Atomic mass} = \left(\frac{\%\text{ abundance isotope 1}}{100}\right) \times (\text{mass of isotope 1}) + \left(\frac{\%\text{ abundance isotope 2}}{100}\right) \times (\text{mass of isotope 2}) \quad + \quad ... \tag{1.9.1}$$

Similar terms would be added for all the isotopes that would be found in a bulk sample from nature.

GPAs

The weighted average is analogous to the method used to calculate grade point averages in most colleges:

$$\text{GPA} = \left(\frac{\text{Credit Hours Course 1}}{\text{total credit hours}}\right) \times (\text{Grade in Course 1}) + \left(\frac{\text{Credit Hours Course 2}}{\text{total credit hours}}\right) \times (\text{Grade in Course 2}) \ + \ ...$$

The periodic table lists the atomic masses of all the elements. Comparing these values with those given for some of the isotopes reveals that the atomic masses given in the periodic table never correspond exactly to those of any of the isotopes Figure 1.9.1. 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:

$$(0.9889 \times 12 \text{ amu}) + (0.0111 \times 13.003355 \text{ amu}) = 12.01 \text{ amu} \tag{1.9.2}$$

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.

5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.99840316	10 Ne Neon 20.180
13 Al Aluminum 26.981538	14 Si Silicon 28.085	15 P Phosphorus 30.97376200	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.9
31 Ga Gallium 69.72	32 Ge Germanium 72.63	33 As Arsenic 74.92159	34 Se Selenium 78.97	35 Br Bromine 79.90	36 Kr Krypton 83.80

Figure 1.9.1: Top three rows of the Periodic Table of Elements that is color coded for atomic mass (from Figure 1.8.2). (PubChem via National Center for Biotechnology Information (2020).

Example 1.9.1: Lead

Naturally occurring lead is found to consist of four isotopes:

- 1.40% $^{204}_{82}\mathrm{Pb}$ whose isotopic mass is 203.973.
- 24.10% $^{206}_{82}\mathrm{Pb}$ whose isotopic mass is 205.974.
- 22.10% $^{207}_{82}\mathrm{Pb}$ whose isotopic mass is 206.976.
- 52.40% $^{208}_{82}\mathrm{Pb}$ whose isotopic mass is 207.977.

Calculate the atomic mass of an average naturally occurring sample of lead.

Solution

This is a direct application of Equation 1.9.1 and is best calculated term by term.

Suppose that you had 1 mol lead. This would contain 1.40% ($\frac{1.40}{100}$ × 1 mol) $^{204}_{82}\mathrm{Pb}$ whose molar mass is 203.973 g mol^{-1}. The mass of $^{204}_{82}\mathrm{Pb}$ would be

$$\begin{aligned} \mathrm{m}_{204} &= n_{204} \times M_{204} \\ &= \left(\frac{1.40}{100} \times 1 \text{ mol}\right) (203.973 \text{ g mol}^{-1}) \\ &= 20.86 \text{ g} \end{aligned}$$

Similarly for the other isotopes

$$\begin{aligned} \mathrm{m}_{206} &= n_{206} \times M_{206} \\ &= \left(\frac{24.10}{100} \times 1 \text{ mol}\right) (205.974 \text{ g mol}^{-1}) \\ &= 490.64 \text{ g} \end{aligned}$$

$$\begin{aligned} \mathrm{m}_{207} &= n_{207} \times M_{207} \\ &= \left(\frac{22.10}{100} \times 1 \text{ mol}\right) (206.976 \text{ g mol}^{-1}) \\ &= 450.74 \text{ g} \end{aligned}$$

$$\begin{aligned} \mathrm{m}_{208} &= n_{208} \times M_{208} \\ &= \left(\frac{52.40}{100} \times 1 \text{ mol}\right) (207.977 \text{ g mol}^{-1}) \\ &= 1080.98 \text{ g} \end{aligned}$$

Upon summing all four results, the mass of 1 mol of the mixture of isotopes is to be found

$$2.86\,g + 49.64\,g + 45.74\,g + 108.98\,g = 207.22\,g$$

The mass of an average lead atom, and thus lead's atomic mass, is 207.2 g/mol. This should be confirmed by consulting the Periodic Table of the Elements.

Exercise 1.9.1: Boron

Boron has two naturally occurring isotopes. In a sample of boron, 20% of the atoms are $\mathrm{B}-10$, which is an isotope of boron with 5 neutrons and mass of $10\,\mathrm{amu}$. The other 80% of the atoms are $\mathrm{B}-11$, which is an isotope of boron with 6 neutrons and a mass of $11\,\mathrm{amu}$. What is the atomic mass of boron?

Answer

The mass of an average boron atom, and thus boron's atomic mass, is $10.8\,\mathrm{amu}$. This should be confirmed by consulting the Periodic Table of the Elements.

But which Natural Abundance should be used?

An important corollary to the existence of isotopes should be emphasized at this point. When highly accurate results are obtained, atomic weights may vary slightly depending on where a sample of an element was obtained. For this reason, the Commission on Isotopic Abundance and Atomic Weights of IUPAC (IUPAC/CIAAWhas redefined the atomic masses of 10 elements having two or more isotopes. The percentages of different isotopes often depends on the source of the element.

For example, oxygen in Antarctic precipitation has an atomic weight of 15.99903, but oxygen in marine N_2O has an atomic mass of 15.9997. *"Fractionation"* of the isotopes results from slightly different rates of chemical and physical processes caused by small differences in their masses. The difference can be more dramatic when an isotope is derived from nuclear reactors.

Mass Spectrometry: Measuring the Mass of Atoms and Molecules

Although the masses of the electron, the proton, and the neutron are known to a high degree of precision, 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 1.9.2). 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.

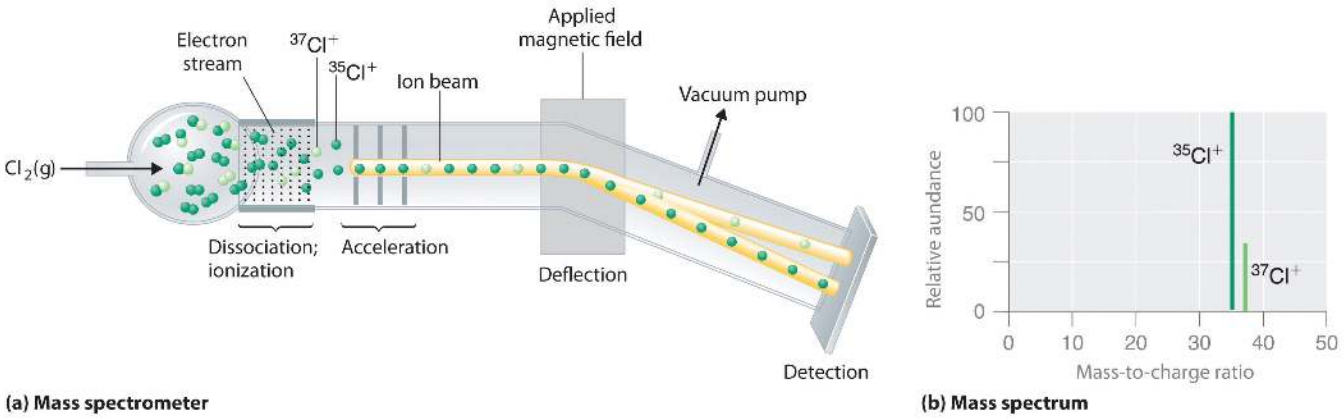


Figure 1.9.2: Determining Relative Atomic Masses Using a Mass Spectrometer. Chlorine consists of two isotopes, ^{35}Cl and ^{37}Cl, in approximately a 3:1 ratio. (a) When a sample of elemental chlorine is injected into the mass spectrometer, electrical energy is used to dissociate the Cl_2 molecules 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 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

$$\frac{\text{mass of } ^{2}\text{H}}{\text{mass of } ^{12}\text{C}} \times \text{mass of } ^{12}\text{C} = 0.167842 \times 12 \text{ amu} = 2.104104 \text{ amu} \tag{1.9.3}$$

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

Example 1.9.2: 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 (Equation 1.9.1. In general, we can write

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

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

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

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

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

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

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

$$40.00 \text{ amu} + 39.90 \text{ amu} = 79.90 \text{ amu}$$

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 1.9.2

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

24.31 amu

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.

Contributors and Attributions

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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1.10: The Origins of Atoms and Elements

The Earth is composed of 90 chemical elements, of which 81 have at least one stable isotope. Most of these elements have also been detected in stars. Where did these elements come from? The accepted scenario is that the first major element to condense out of the primordial soup was helium, which still comprises about one-quarter of the mass of the known universe.

Stellar nucleosynthesis is the generation of new elements by nuclear reaction within stars. According to the **Big bang theory** for which there is now overwhelming evidence, the universe as we know it had its origin in a point source or **singularity** that began an explosive expansion about 12-15 billion years ago, and which is still continuing. Following a brief period of extremely rapid expansion. Helium and hydrogen became stable during the first few minutes, along with some of the very lightest nuclides up to lithium, which were formed through various nuclear reaction. Formation of most heavier elements was delayed for about million years until nucleosynthesis commenced in the first stars. Hydrogen still accounts for about 93% of the atoms in the universe.

All elements beyond hydrogen were formed in regions where the concentration of matter was large, and the temperature was high; in other words, in stars. The formation of a star begins when the gravitational forces due to a large local concentration of hydrogen bring about a contraction and compression to densities of around 10^5 g cm^{-3}. This is a highly exothermic process in which the gravitational potential energy is released as heat, about 1200 kJ per gram, raising the temperature to about 10^7 K. Under these conditions, hydrogen nuclei possess sufficient kinetic energy to overcome their electrostatic repulsion and undergo nuclear fusion to generate helium (Figure 1.10.1). This is known as "**hydrogen burning**".

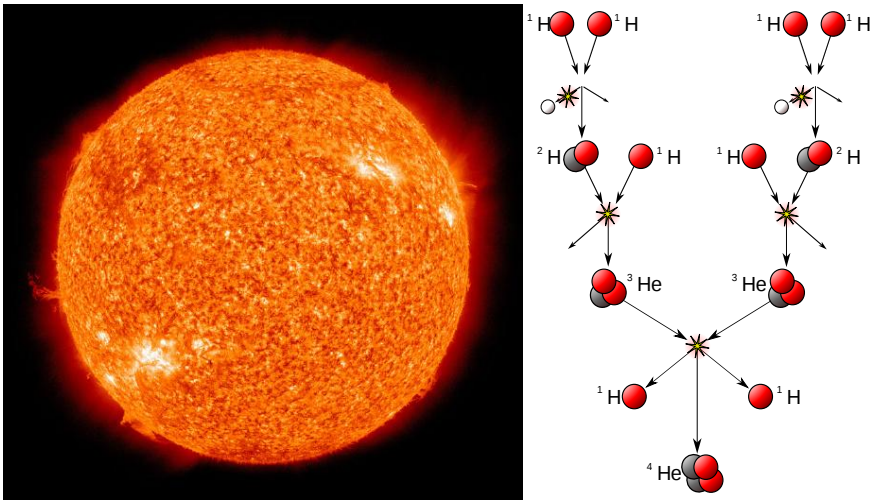


Figure 1.10.1: (left) The intense pressure and temperature of stars are sufficient to force nuclei to fuse to generate heavier elements. (Public Domain; NASA) (Public Domain; NASA) (right) Hydrogen burning nuclear reactions in stars to generate helium from hydrogen. Many other burning reactions occur in stars to generate the heavier elements of the universe. (CC BY-SA 3.0; Borb via Wikipedia)

As hydrogen burning proceeds, the helium collects in the core of the star, raising the density to 10^8 g cm^{-3} and the temperature to 10^8 K. This temperature is high enough to initiate **helium burning**. The size of a star depends on the balance between the kinetic energy of its matter and the gravitational attraction of its mass. As the helium burning runs its course, the temperature drops and the star begins to contract. The course of further nucleosynthesis event and the subsequent fate of the star itself depends on the star's mass. Fusion into heavier species than iron is also precluded by the electrostatic repulsion of the highly charged nuclei. However,further nuclear processes are responsible for these.

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CHAPTER OVERVIEW

2: Matter, Measurement, and Problem Solving

2.1: The Metric Mix-up - A $327 Million Unit Error
2.2: The Reliability of a Measurement
2.3: Density
2.4: Energy and Its Units
2.5: Converting between Units
2.6: Problem-Solving Strategies
2.7: Solving Problems Involving Equations
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2.1: The Metric Mix-up - A $327 Million Unit Error

Small errors in these unit systems can sometimes harbor massive ramifications. Although NASA declared the metric system as its official unit system in the 1980s, conversion factors remain an issue. The Mars Climate Orbiter, meant to help relay information back to Earth, is one notable example of the unit system struggle. The orbiter was part of the Mars Surveyor ’98 program, which aimed to better understand the climate of Mars.

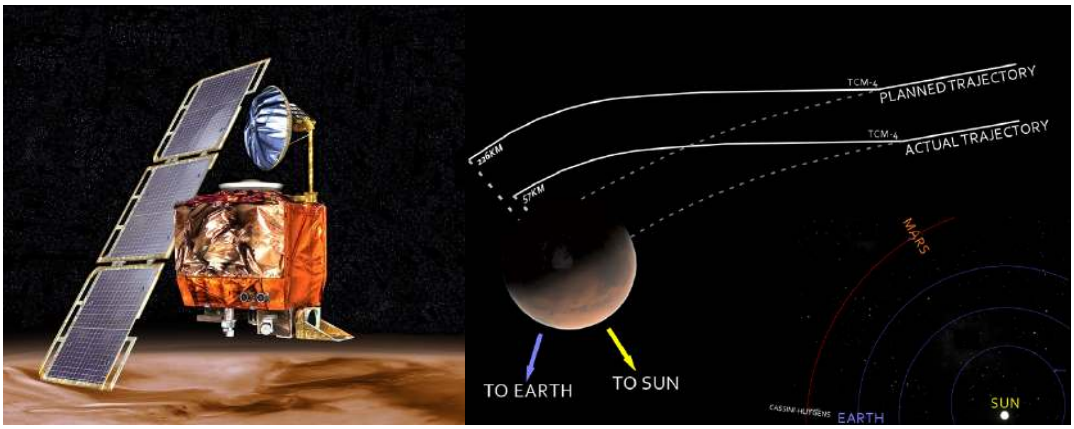


Figure 2.1.1: (left) The Mars Climate Orbiter, (Public Domain; NASA/JPL-Caltech). (right) Diagram of the mishap during the Mars Climate Orbiter mission that resulted in the loss of the spacecraft. (CC BY-SA 3.0; Xession via Wikipedia)

As the spacecraft journeyed into space on September 1998, it should have entered orbit at an altitude of 140-150 km above Mars, but instead went as close as 57 km. This navigation error occurred because the software that controlled the rotation of the craft’s thrusters was not calibrated in SI units. The spacecraft expected newtons, while the computer, which was inadequately tested, worked in pound-forces; one pound force is equal to about 4.45 newtons. Unfortunately, friction and other atmospheric forces destroyed the Mars Climate Orbiter.

Clearly, the 4.45-fold difference between the newtons and foot-pound units is catastrophic for space exploration. The project cost $327.6 million in total. Tom Gavin, an administrator for NASA's Jet Propulsion Laboratory in Pasadena, stated, "This is an end-to-end process problem. A single error like this should not have caused the loss of Climate Orbiter. Something went wrong in our system processes in checks and balances that we have that should have caught this and fixed it." As most advanced chemistry students can attest, properly using units are similarly critical in chemistry; failure to address them properly can have dire consequences.

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2.2: The Reliability of a Measurement

Learning Objectives

- Define accuracy and precision
- Distinguish exact and uncertain numbers
- Correctly represent uncertainty in quantities using significant figures
- Apply proper rounding rules to computed quantities

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an exact number. If we count eggs in a carton, we know *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

Reporting Measurements to Reflect Certainty

Scientific measurements are of no value (or at least, they're not really *scientific*) unless they are given with some statement of the errors they contain. If a poll reports that one candidate leads another by 5%, that may be *politically* useful for the winning candidate to point out. But all respectable polls are *scientific*, and report errors. If the error in measurement is plus or minus 10%, which indicates anything from the candidate leading by 15% to trailing by 5%, the poll really does not reliably tell who is in the lead. If the poll had an error of 1%, the leading candidate could make a more scientific case that for being in the lead (by a 4% to 6% margin, or 5% +/-1%).

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. Scientific measurements are reported so that every digit is certain except the last, which is estimated. All digits of a measured quantity, including the certain one, are called significant figures.

To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

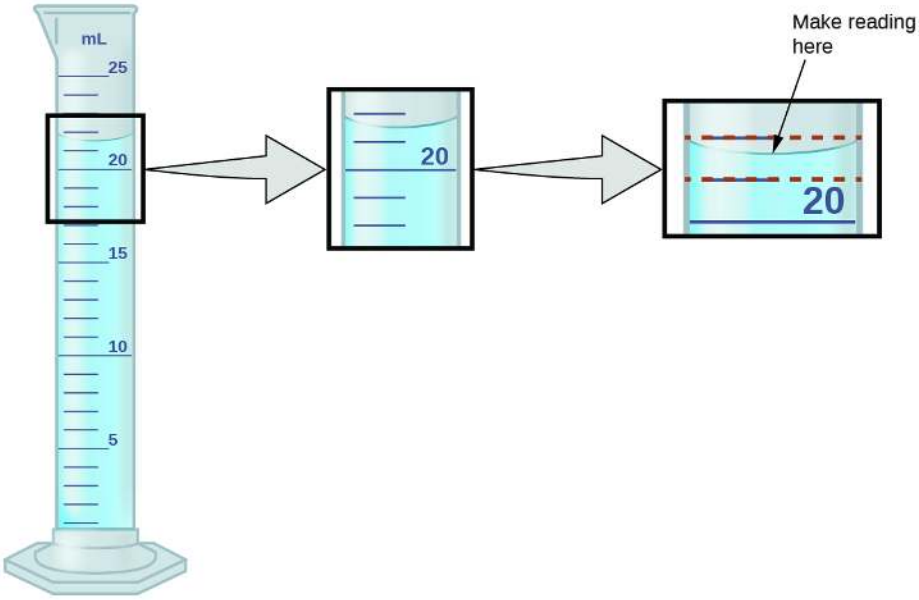


Figure 2.2.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in Figure 2.2.1. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

Example 2.2.1

How much water (with yellow dye) does the graduated buret in Figure 2.2.2 contain?



Figure 2.2.2: A meniscus as seen in a burette of colored water.

Solution

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.

This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of ± 0.01 gram. If we weigh the quarter on a more sensitive balance, we may find that its mass is 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram. Every measurement has some uncertainty, which depends on the device used (and the user's ability). All of the digits in a measurement, including the uncertain last digit, are called significant figures or significant digits. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 2.2.2).

Figure 2.2.1 help to understand the difference between precision (small expected difference between multiple measurements) and accuracy (difference between the result and a known value).

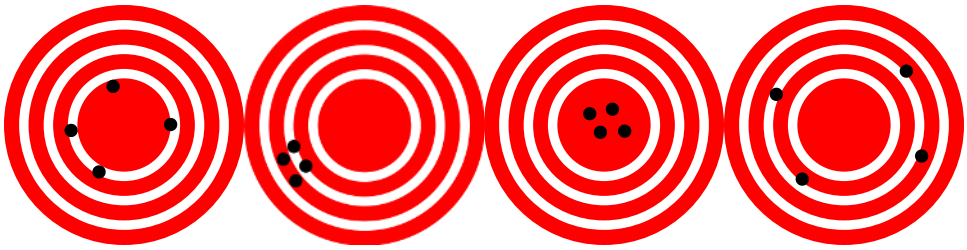


Figure 2.2.1: (left) High accuracy and Low Precision. (middle left) Low accuracy and High precision. (middle right) High accuracy and Low Precision. (middle left) Low accuracy and Low precision(Public Domain; DarkEvil)

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 2.2.2.

Table 2.2.2: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

Summary

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

Glossary

uncertainty
: estimate of amount by which measurement differs from true value

significant figures
: (also, significant digits) all of the measured digits in a determination, including the uncertain last digit

rounding
: procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

precision
: how closely a measurement matches the same measurement when repeated

exact number

number derived by counting or by definition

accuracy

how closely a measurement aligns with a correct value

Contributors and Attributions

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2.3: Density

Learning Objectives

- Define density
- Use density as a conversion factor

The terms *heavy* and *light* are commonly used in two different ways. We refer to weight when we say that an adult is heavier than a child. On the other hand, something else is alluded to when we say that oak is heavier than balsa wood. A small shaving of oak would obviously weigh less than a roomful of balsa wood, but oak is heavier in the sense that a piece of given size weighs more than the same-size piece of balsa.

What we are actually comparing is the *mass per unit volume*, that is, the **density**. In order to determine these densities, we might weigh a cubic centimeter of each type of wood. If the oak sample weighed 0.71 g and the balsa 0.15 g, we could describe the density of oak as 0.71 g cm^{-3} and that of balsa as 0.15 g cm^{-3}. (Note that the negative exponent in the units cubic centimeters indicates a reciprocal. Thus 1 cm^{-3} = 1/cm^3 and the units for our densities could be written as $\frac{g}{cm^3}$, g/cm^3, or g cm^{-3}. In each case the units are read as grams per cubic centimeter, the *per* indicating division.) We often abbreviate "cm^3" as "cc", and 1 cm^3 = 1 mL exactly by definition.

In general it is not necessary to weigh exactly 1 cm^3 of a material in order to determine its density. We simply measure mass and volume and divide volume into mass:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \tag{2.3.1}$$

or

$$\rho = \frac{m}{V} \tag{2.3.2}$$

where ρ is density, m is mass, and V is the volume.

Example 2.3.1: Density of Aluminum

Calculate the density of:

a. a piece of aluminum whose mass is 37.42 g and which, when submerged, increases the water level in a graduated cylinder by 13.9 ml;
b. an aluminum cylinder of mass 25.07 g, radius 0.750 cm, and height 5.25 cm.

Solution

a) Since the submerged metal displaces its own volume,

$$\begin{aligned}\text{Density} = \rho &= \frac{m}{V} \\ &= \frac{37.42\ \text{g}}{13.9\ \text{ml}} \\ &= 2.69\ \text{g/ml or } 2.69\ \text{g ml}^{-1}\end{aligned}$$

b) The volume of the cylinder must be calculated first, using the formula

$$\begin{aligned}\text{V} &= \pi r^2 h \\ &= 3.142 \times (0.750\ \text{cm})^2 \times 5.25\ \text{cm} \\ &= 9.278\ \text{cm}^3\end{aligned}$$

Then

$$\rho = \frac{m}{V} = \frac{25.07\ \text{g}}{9.278\ \text{cm}^3} = \begin{cases} 2.70 \dfrac{\text{g}}{\text{cm}^3} \\ 2.70\ \text{g cm}^{-3} \\ 2.70\ \text{g/cm}^3 \end{cases}$$

which are all acceptable alternatives.

Note that unlike mass or volume (**extensive properties**), the density of a substance is independent of the size of the sample (**intensive property**). Thus density is a property by which one substance can be distinguished from another. A sample of pure aluminum can be trimmed to any desired volume or adjusted to have any mass we choose, but its density will always be 2.70 g/cm^3 at 20°C. The densities of some common pure substances are listed below.

Tables and graphs are designed to provide a maximum of information in a minimum of space. When a physical quantity (number × units) is involved, it is wasteful to keep repeating the same units. Therefore it is conventional to use pure numbers in a table or along the axes of a graph. A pure number can be obtained from a quantity if we divide by appropriate units. For example, when divided by the units gram per cubic centimeter, the density of aluminum becomes a pure number 2.70:

$$\frac{\text{Density of aluminum}}{1\ \text{g cm}^{-3}} = \frac{2.70\ \text{g cm}^{-3}}{1\ \text{g cm}^{-3}} = 2.70$$

Table 2.3.1: Density of Several Substances at 20°C.Anchor

Substance	Density / g cm^{-3}
Helium gas	0.000 16
Dry air	0.001 185
Gasoline	0.66-0.69 (varies)
Kerosene	0.82
Benzene	0.880
Water	1.000
Carbon tetrachloride	1.595
Magnesium	1.74
Salt	2.16
Aluminum	2.70
Iron	7.87
Copper	8.96
Silver	10.5
Lead	11.34
Uranium	19.05
Gold	19.32

Therefore, a column in a table or the axis of a graph is conveniently labeled in the following form:

Quantity/units

This indicates the units that must be divided into the quantity to yield the pure number in the table or on the axis. This has been done in the second column of the table.

Converting Densities

In our exploration of density, notice that chemists may express densities differently depending on the subject. The density of pure substances may be expressed in kg/m^3 in some journals which insist on strict compliance with SI units; densities of soils may be expressed in lb/ft^3 in some agricultural or geological tables; the density of a cell may be expressed in mg/µL; and other units are in common use. It is easy to transform densities from one set of units to another, by multiplying the original quantity by one or more ***unity factors***:

Example 2.3.2: Density of Water

Convert the density of water, 1 g/cm^3 to (a) lb/cm^3 and (b) lb/ft^3

Solution

a. The equality $454\ \text{g} = 1\ \text{lb}$ can be used to write two unity factors,

$$\frac{454\ \text{g}}{1\ \text{lb}}$$

or

$$\frac{1\ \text{lb}}{454\ \text{g}}$$

The given density can be multiplied by one of the unity factors to get the desired result. The correct conversion factor is chosen so that the units cancel:

$$1\frac{\text{g}}{\text{cm}^3} \times \frac{1\ \text{lb}}{454\ \text{g}} = 0.002203\frac{\text{lb}}{\text{cm}^3}$$

b. Similarly, the equalities $2.54\ \text{cm} = 1\ \text{inch}$, and $12\ \text{inches} = 1\ \text{ft}$ can be use to write the unity factors:

$$\frac{2.54\ \text{cm}}{1\ \text{in}}, \frac{1\ \text{in}}{2.54\ \text{cm}}, \frac{12\ \text{in}}{1\ \text{ft}}\ \text{and}\ \frac{1\ \text{ft}}{12\ \text{in}}$$

In order to convert the cm^3 in the denominator of 0.002203 to in^3, we need to multiply by the appropriate unity factor three times, or by the cube of the unity factor:

$$0.002203\frac{\text{g}}{\text{cm}^3} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{2.54\ \text{cm}}{1\ \text{in}}$$

or

$$0.002203\frac{\text{g}}{\text{cm}^3} \times \left(\frac{2.54\ \text{cm}}{1\ \text{in}}\right)^3 = 0.0361\ \text{lb/in}^3$$

This can then be converted to lb/ft^3:

$$0.0361\ \text{lb/in}^3 \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^3 = 62.4\ \text{lb/ft}^3$$

It is important to notice that we have used conversion factors to convert from one unit to another unit of the **same parameter**

Contributors and Attributions

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2.4: Energy and Its Units

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 2.4.1). 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.

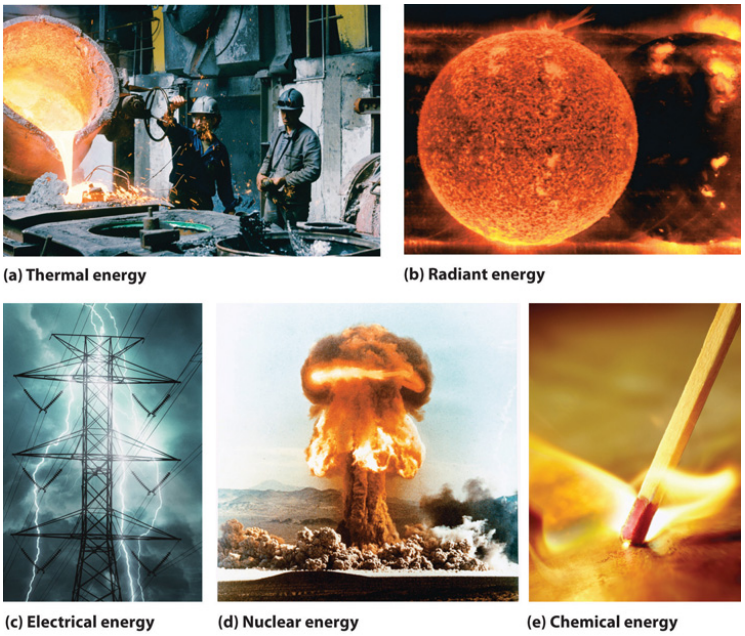


Figure 2.4.1: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, 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 2.4.2) 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 2.4.2: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work (Figure 2.4.3), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

work = force x distance

$$w = F\,d \tag{2.4.1}$$

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), we can also write Equation 2.4.1 as follows:

work= mass x acceleration x distance

$$w = m\,a\,d \tag{2.4.2}$$

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (*w*) and thus the energy required depends on three things:

1. the height of the second floor (the distance *d*);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

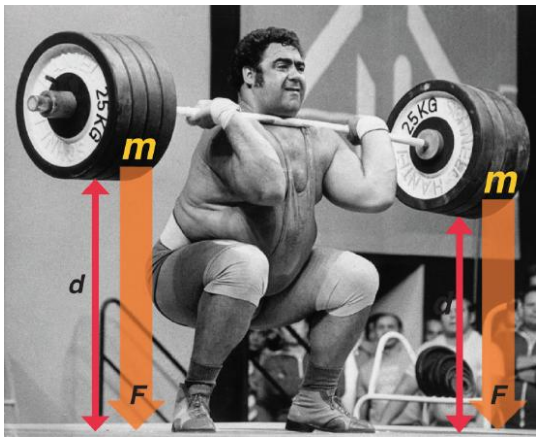


Figure 2.4.2: An Example of Mechanical Work. One form of energy is mechanical work, the energy required to move an object of mass *m* a distance *d* when opposed by a force *F*, such as gravity.

In contrast, heat (*q*) is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature.

Energy is an *extensive* property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pan of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker. We now present a more detailed description of kinetic and potential energy.

Kinetic and Potential Energy

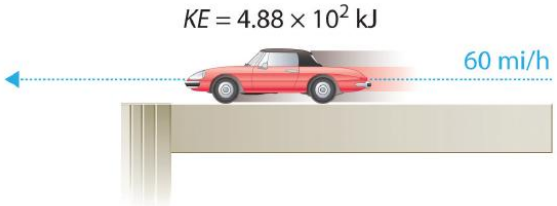
The kinetic energy of an object is related to its mass m and velocity v:

$$KE = \frac{1}{2}mv^2 \tag{2.4.3}$$

For example, the kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) is

$$KE = \frac{1}{2}(1360kg)(26.8ms)^2 = 4.88 \times 10^5 g \cdot m^2 \tag{2.4.4}$$

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule (1818–1889), an early worker in the field of energy. is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × 10^5 J or 4.88 × 10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.



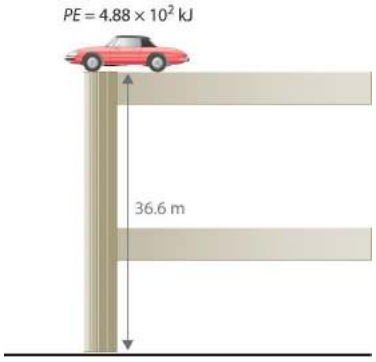
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is *w* = *Fd*. According to Equation 2.4.2, 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:

$$PE = F\ d = m\ a\ d = m\ g\ h \tag{2.4.5}$$

$$PE = (1360, Kg)\left(\frac{9.81\ m}{s^2}\right)(36.6\ m) = 4.88 \times 10^5\ \frac{Kg \cdot m}{s^2} \tag{2.4.6}$$

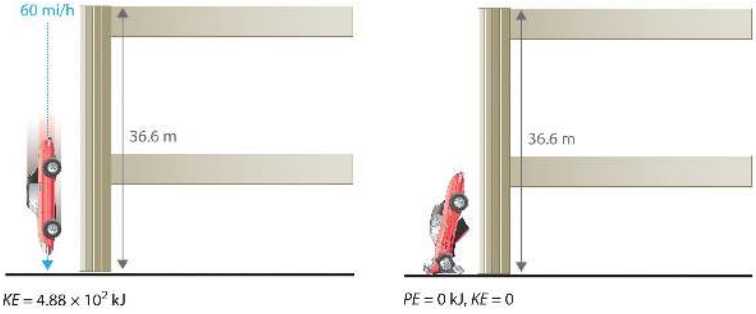
$$= 4.88 \times 10^5 J = 488\ kJ \tag{2.4.7}$$

The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.



If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.

Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.



When the car is falling from the top of the parking structure it has a kinetic energy of 488 kilojoules. When the car hits the floor is has a potential and kinetic energy of zero.

Units of Energy

The units of energy are the same for all forms of energy. Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C. The name is derived from the Latin *calor*, meaning “heat.” Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal = 4.184\ J \text{ exactly} \tag{2.4.8}$$

$$1\ J = 0.2390\ cal \tag{2.4.9}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

Example 2.4.1

a. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
b. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Given: mass and velocity or height

Asked for: kinetic and potential energy

Strategy:

Use Equation 5.1.4 to calculate the kinetic energy and Equation 5.1.6 to calculate the potential energy, as appropriate.

Solution:

a. The kinetic energy of an object is given by $\frac{1}{2}mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units:

$$v = \left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right) = 44.7\ m/s$$

The kinetic energy of the baseball is therefore

$$KE = 1492\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2 = 1.49 \times 10^2\ \frac{kg \cdot m^2}{s^2} = 1.49 \times 10^2\ J$$

b. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 − 3) = 247 feet above its initial position. Thus

$$PE = 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)(247\ \cancel{ft})\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right) = 1.10 \times 10^2$$

$$\frac{kg \cdot m^2}{s^2} = 1.10 \times 10^2\ J$$

Exercise 2.4.1

a. In a bowling alley, the distance from the foul line to the head pin is 59 ft, 10 13/16 in. (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
b. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer a

3.10×10^2 J

Answer 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. The most common units of energy are the **joule (J)**, defined as 1

$(kg \cdot m^2)/s^2$, 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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2.5: Converting between Units

Learning Objectives

- To convert a value reported in one unit to a corresponding value in a different unit using conversion factors.

Earlier we showed how unity factors can be used to express quantities in different units of the same parameter. For example, a density can be expressed in g/cm^3 or lb/ft^3. Now we will see how *conversion factors* representing mathematical functions, like $\rho = m/V$, can be used to transform quantities into different parameters. For example, what is the volume of a given *mass* of gold? Unity factors and conversion factors are conceptually different, and we'll see that the "dimensional analysis" we develop for unit conversion problems must be used with care in the case of functions.

Conversion Factors

A **conversion factor** is a factor used to convert one unit of measurement into another. A simple conversion factor can be used to convert meters into centimeters, or a more complex one can be used to convert miles per hour into meters per second. Since most calculations require measurements to be in certain units, you will find many uses for conversion factors. What always must be remembered is that a conversion factor has to represent a fact; this fact can either be simple or much more complex. For instance, you already know that 12 eggs equal 1 dozen. A more complex fact is that the speed of light is 1.86×10^5 miles/sec. Either one of these can be used as a conversion factor depending on what type of calculation you might be working with (Table 2.5.1).

Table 2.5.1: Conversion Factors from SI units to English Units

English Units	Metric Units	Quantity
1 ounce (oz)	28.35 grams (g)	*mass
1 fluid once (oz)	29.6 mL	volume
2.205 pounds (lb)	1 kilogram (kg)	*mass
1 inch (in)	2.54 centimeters (cm)	length
0.6214 miles (mi)	1 kilometer (km)	length
1 quarter (qt)	0.95 liters (L)	volume

*pounds and ounces are technically units of force, not mass.

Of course, there are other ratios which are not listed in Table 2.5.1. They may include:

- Ratios embedded in the text of the problem (using words such as *per* or *in each*, or using symbols such as / or %).
- Conversions in the metric system, as covered earlier in this chapter.
- Common knowledge ratios (such as 60 seconds = 1 minute).

If you learned the SI units and prefixes described, then you know that 1 cm is 1/100th of a meter.

$$1\text{ cm} = \frac{1}{100}\text{ m} = 10^{-2}\text{m}$$

or

$$100\text{ cm} = 1\text{ m}$$

Suppose we divide both sides of the equation by 1m (both the number *and* the unit):

$$\frac{100\text{ cm}}{1\text{ m}} = \frac{1\text{ m}}{1\text{ m}}$$

As long as we perform the same operation on both sides of the equals sign, the expression remains an equality. Look at the right side of the equation; it now has the same quantity in the numerator (the top) as it has in the denominator (the bottom). Any fraction

that has the same quantity in the numerator and the denominator has a value of 1:

$$\frac{100\text{ cm}}{1\text{ m}} = \frac{1000\text{ mm}}{1\text{ m}} = \frac{1 \times 10^6 \mu\text{m}}{1\text{ m}} = 1$$

We know that 100 cm *is* 1 m, so we have the same quantity on the top and the bottom of our fraction, although it is expressed in different units.

Dimensional Analysis

Dimensional analysis is amongst the most valuable tools physical scientists use. Simply put, it is the conversion between an amount in one unit to the corresponding amount in a desired unit using various conversion factors. This is valuable because certain measurements are more accurate or easier to find than others. The use of units in a calculation to ensure that we obtain the final proper units is called **dimensional analysis**.

Here is a simple example. How many centimeters are there in 3.55 m? Perhaps you can determine the answer in your head. If there are 100 cm in every meter, then 3.55 m equals 355 cm. To solve the problem more formally with a conversion factor, we first write the quantity we are given, 3.55 m. Then we multiply this quantity by a conversion factor, which is the same as multiplying it by 1. We can write 1 as $\frac{100\text{ cm}}{1\text{ m}}$ and multiply:

$$3.55\text{ m} \times \frac{100\text{ cm}}{1\text{ m}}$$

The 3.55 m can be thought of as a fraction with a 1 in the denominator. Because m, the abbreviation for meters, occurs in both the numerator *and* the denominator of our expression, they cancel out:

$$\frac{3.55\ \cancel{\text{m}}}{1} \times \frac{100\text{ cm}}{1\ \cancel{\text{m}}}$$

The final step is to perform the calculation that remains once the units have been canceled:

$$\frac{3.55}{1} \times \frac{100\text{ cm}}{1} = 355\text{ cm}$$

In the final answer, we omit the 1 in the denominator. Thus, by a more formal procedure, we find that 3.55 m equals 355 cm. A generalized description of this process is as follows:

$$\text{quantity } \cancel{\text{(old units)}} \times \underbrace{\left(\frac{\text{new units}}{\cancel{\text{old units}}}\right)}_{\text{conversion factor}=1} = \text{quantity (new units)} \tag{2.5.1}$$

You may be wondering why we use a seemingly complicated procedure for a straightforward conversion. In later studies, the conversion problems you will encounter *will not always be so simple*. If you can master the technique of applying conversion factors, you will be able to solve a large variety of problems.

In the previous example, we used the fraction $\frac{100\text{ cm}}{1\text{ m}}$ as a conversion factor. Does the conversion factor $\frac{1\text{ m}}{100\text{ cm}}$ also equal 1? Yes, it does; it has the same quantity in the numerator as in the denominator (except that they are expressed in different units). Why did we not use *that* conversion factor? If we had used the second conversion factor, the original unit would not have canceled, and the result would have been meaningless. Here is what we would have gotten:

$$3.55\text{ m} \times \frac{1\text{ m}}{100\text{ cm}} = 0.0355\frac{\text{m}^2}{\text{cm}}$$

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out.* Figure 2.5.1 shows a concept map for constructing a proper conversion.

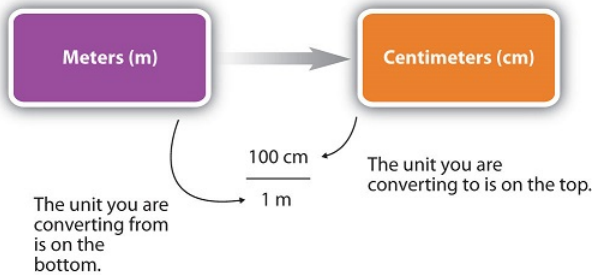


Figure 2.5.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another.

? Exercise 2.5.1

Perform each conversion.

a. 101,000. ns to seconds
b. 32.08 kg to grams
c. 1.53 grams to cg

Answer a

$1.01000 \times 10^{-4} s$

Answer b

$3.208 \times 10^{4} g$

Answer c

$1.53 \times 10^{2} g$

Summary

- Conversion factors are used to convert one unit of measurement into another.
- Dimensional analysis (unit conversions) involves the use of conversion factors that will cancel units you don't want and produce units you do want.

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2.6: Problem-Solving Strategies

We know the conversion factor is correct when units cancel appropriately, but a conversion factor is not unity, however. Rather it is a physical quantity (or the reciprocal of a physical quantity) which is related to the two other quantities we are interconverting. The conversion factor works because of the relationship, *not* because it is has a value of one. Once we have established that a relationship exists, it is no longer necessary to memorize a mathematical formula. The units tell us whether to use the conversion factor or its reciprocal. Without such a relationship, however, mere cancellation of units does not guarantee that we are doing the right thing.

A simple way to remember relationships among quantities and conversion factors is a “road map“of the type shown below:

$$\text{Mass} \overset{density}{\longleftrightarrow} \text{volume or } m \overset{\rho}{\longleftrightarrow} V \tag{2.6.1}$$

This indicates that the mass of a particular sample of matter is related to its volume (and the volume to its mass) through the conversion factor, density. The double arrow indicates that a conversion may be made in either direction, provided the units of the conversion factor cancel those of the quantity which was known initially. In general the road map can be written

$$\text{First quantity} \overset{\text{conversion factor}}{\longleftrightarrow} \text{second quantity} \tag{2.6.2}$$

General Steps in Performing Dimensional Analysis

1. Identify the "**given**" information in the problem. Look for a number with units to start this problem with.
2. What is the problem asking you to "**find**"? In other words, what unit will your answer have?
3. Use **ratios** and conversion factors to cancel out the units that aren't part of your answer, and leave you with units that are part of your answer.
4. When your units cancel out correctly, you are ready to do the **math**. You are multiplying fractions, so you multiply the top numbers and divide by the bottom numbers in the fractions.

As we come to more complicated problems, where several steps are required to obtain a final result, such road maps will become more useful in charting a path to the solution.

Example 2.6.1: Volume to Mass Conversion

Black ironwood has a density of 67.24 lb/ft^3. If you had a sample whose volume was 47.3 ml, how many grams would it weigh? (1 lb = 454 g; 1 ft = 30.5 cm).

Solution

The road map

$$V \overset{\rho}{\rightarrow} m$$

tells us that the mass of the sample may be obtained from its volume using the conversion factor, density. Since milliliters and cubic centimeters are the same, we use the SI units for our calculation:

$$\text{Mass} = m = 47.3\text{cm}^3 \times \frac{67.24 \text{ lb}}{1 \text{ ft}^3}$$

Since the volume units are different, we need a unity factor to get them to cancel:

$$m = 47.3 \text{ cm}^3 \times \left(\frac{1 \text{ ft}}{30.5 \text{ cm}}\right)^3 \times \frac{67.24 \text{ lb}}{1 \text{ ft}^3} = 47.3 \text{ cm}^3 \times \frac{1 \text{ ft}^3}{30.5^3 \text{ cm}^3} \times \frac{67.24 \text{ lb}}{1 \text{ ft}^3}$$

We now have the mass in pounds, but we want it in grams, so another unity factor is needed:

$$m = 47.3 \text{ cm}^3 \times \frac{1 \text{ ft}^3}{30.5^3 \text{ cm}^3} \times \frac{67.24 \text{ lb}}{1 \text{ ft}^3} \times \frac{454 \text{ g}}{1 \text{ lb}} = 500.9 \text{ g}$$

In subsequent chapters we will establish a number of relationships among physical quantities. Formulas will be given which define these relationships, but we do not advocate slavish memorization and manipulation of those formulas. Instead we recommend that you remember that a relationship exists, perhaps in terms of a road map, and then adjust the quantities involved so that the units cancel appropriately. Such an approach has the advantage that you can solve a wide variety of problems by using the same technique.

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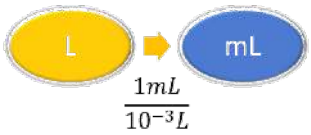
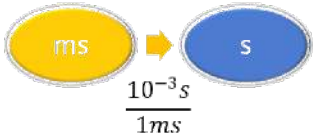
2.7: Solving Problems Involving Equations

Many problems in chemistry involve manipulating equations and require the use of multiple conversion steps. Such problems easy to solve as numerical problems once you understand how to approach them. The four simple steps in problem solving are READ-PLAN-SOLVE-CHECK approach.

Steps to Solve Chemistry Problems

1. **READ** the question: Before you start calculating and manipulating equations, **read** the complete problem thoroughly to ensure you understand what being asked.
2. **PLAN** your approach:
   - Write down all of the information you have been given. It is not uncommon that problems will give more facts than are required to solve - this is a bit of reality in the problem.
   - Identify the equation(s) that are required to use to solve the problem, this often requires manipulating one or more equations to give you the desired answer.
3. **SOLVE** the problem
   - Before calculating results, **confirm the correct units** required for the equations. You may often are required perform one or more unit conversions before directly using the equations.
   - Insert the relevant parameters into the equation(s) and get your answer. Do not forget that most answers will involve units.
4. **CHECK** your answer: Confirm that you have answered all that is requested in the problem and that the answer seems reasonable. For example, if you are calculating the volume of a sample and your calculated results in cubic kilometers, you probably made an error in a conversion or calculation (unless you are working in an astronomy class).

Example 2.7.1

	Example 2.7.1	**Example** 2.7.2
Steps for Problem Solving	The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?	A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?
Identify the "given"information and what the problem is asking you to "find."	Given: 4.7 L Find: mL	Given: 18 ms Find: s
List other known quantities	$1\,mL = 10^{-3} L$	$1\,ms = 10^{-3} s$
Prepare a concept map and use the proper conversion factor.	 $\frac{1mL}{10^{-3}L}$	 $\frac{10^{-3}s}{1ms}$
Cancel units and calculate.	$4.7\cancel{L} \times \frac{1\text{ mL}}{10^{-3}\ \cancel{L}} = 4,700\text{ mL}$ or $4.7\cancel{L} \times \frac{1,000\text{ mL}}{1\ \cancel{L}} = 4,700\text{ mL}$	$18\ \cancel{\text{ms}} \times \frac{10^{-3}\text{ s}}{1\ \cancel{\text{ms}}} = 0.018\text{ s}$ or $18\ \cancel{\text{ms}} \times \frac{1\text{ s}}{1,000\ \cancel{\text{ms}}} = 0.018\text{ s}$
Think about your result.	The amount in mL should be 1000 times larger than the given amount in L.	The amount in s should be 1/1000 the given amount in ms.

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2.8: Atoms and the Mole - How Many Particles?

Dalton's theory that each chemical compound has a particular combination of atoms and that the ratios of the numbers of atoms of the elements present are usually small whole numbers. It also describes the law of multiple proportions, which states that the ratios of the masses of elements that form a series of compounds are small whole numbers. The problem for Dalton and other early chemists was to discover the quantitative relationship between the number of atoms in a chemical substance and its mass. Because the masses of individual atoms are so minuscule (on the order of 10^{-23} g/atom), chemists do not measure the mass of individual atoms or molecules. In the laboratory, for example, the masses of compounds and elements used by chemists typically range from milligrams to grams, while in industry, chemicals are bought and sold in kilograms and tons. To analyze the transformations that occur between individual atoms or molecules in a chemical reaction, it is therefore essential for chemists to know how many atoms or molecules are contained in a measurable quantity in the laboratory—a given mass of sample.

The Mole: A Chemistry "Dozen"

Because atoms and molecules are extremely small, there are a great many of them in any macroscopic sample. For example a 1 cm^3 of mercury would contain 4.080×10^{22} mercury atoms. The very large numbers involved in counting microscopic particles are inconvenient to think about or to write down. Chemists have chosen to count atoms and molecules using a unit called the **mole** (mol), from the Latin *moles*, meaning "pile" or "heap." One mole is 6.022 x 10^{23} of the microscopic particles which make up the substance in question. Thus 6.022 x 10^{23} Br atoms is referred to as 1 mol Br.

The mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$. This is a fundamental constant named **Avogadro's number** (N_A) or the **Avogadro constant** in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of "per mole," a conveniently rounded version being $6.022 \times 10^{23}/\text{mol}$.

Using Units of Specific Number of Items is Common

Many familiar items are sold in numerical quantities with distinct names. For example, cans of soda come in a six-pack, eggs are sold by the dozen (12), and pencils often come in a gross (12 dozen, or 144). Sheets of printer paper are packaged in reams of 500, a seemingly large number. Atoms are so small, however, that even 500 atoms are too small to see or measure by most common techniques. Any readily measurable mass of an element or compound contains an extraordinarily large number of atoms, molecules, or ions, so an extremely large numerical unit is needed to count them.



Figure 2.8.1: Examples of using a specific number as a unit of measurement.

There is a difference in degree, however, because the mole of anything (6.022 x 10^{23}) is so large. A stack of paper containing a mole of sheets would extend more than a million times the distance from the earth to the sun, and 6.022 x 10^{23} grains of sand would cover all the land in the world to a depth of nearly 2 ft. Obviously there are a great many particles in a mole of anything.

A mole is formally defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. Consistent with this definition, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass of an element (or compound as we will demonstrate) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (Figure 2.8.2).

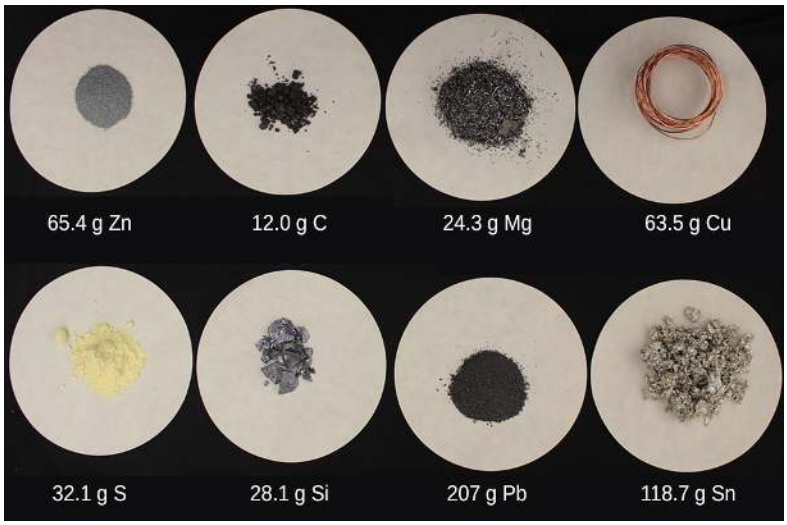


Figure 2.8.2: Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic mass in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C (Table 2.8.1).

Table 2.8.1: Mass of one mole of elements

Element	Average Atomic Mass (amu)	Atomic Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022×10^{23}
H	1.008	1.008	6.022×10^{23}
O	16.00	16.00	6.022×10^{23}
Na	22.99	22.99	6.022×10^{23}
Cl	33.45	35.45	6.022×10^{23}

Overview of Origin and Properties of the Mole

The word "mole" suggests a small, furry burrowing animal to many. But in this lesson, we look at the concept of the mole in chemistry. Learn the incredible magnitude of the mole--and how something so big can help us calculate the tiniest particles in the world.



Video 2.8.1: How big is a mole? (Not the animal, the other one). Lesson by Daniel Dulek, animation by Augenblick Studios.

Converting between Number of Moles and Number of Atoms

Although chemists usually work with moles as units, occasionally it is helpful to refer to the actual number of atoms or molecules involved. When this is done, the symbol N is used for the number of species and n is used for the number of moles. For example, in referring to 1 mol of helium atoms, we could write

$$n_{\mathrm{He}} = 1\mathrm{mol}$$

and

$$N_{\mathrm{He}} = 6.022 \times 10^{23}$$

Obtaining N requires the use of a conversion factor to obtain, which is just N_A. This which is defined by the equation

$$N_{\mathrm{A}} = \frac{N}{n} \tag{2.8.1}$$

Since for any substance there are 6.022×10^{23} particles per mole, Equation 2.8.1 can be expanded:

$$N_{\mathrm{A}} = \frac{6.022 \cdot 10^{23}}{1\ \mathrm{mol}} = 6.022 \times 10^{23}\ \mathrm{mol}^{-1} \tag{2.8.2}$$

Equation 2.8.2 is the most important conversion factor in general chemistry. Figure 2.8.3 is a flowchart for converting between the number of moles and the number of atoms. The use of these conversions is illustrated in Example 2.8.1 and Exercise 2.8.1.

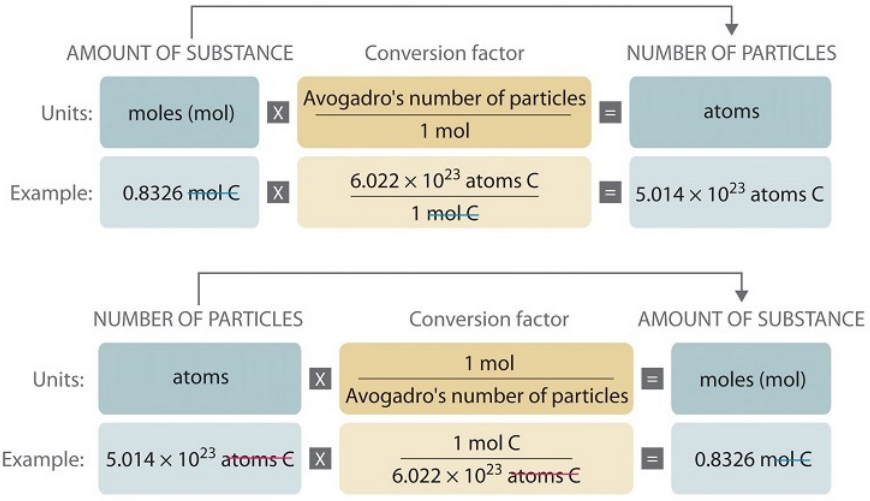


Figure 2.8.3: Forward and Reverse Flowcharts for Converting between the Number of Moles and the Number of Atoms (CC BY-NC-SA 3.0; anonymous)

Example 2.8.1: Copper Atoms

How many atoms are present in 2.76 mol of copper atoms?

Solution

The definition of a mole is an equality that can be used to construct a conversion factor.

$$2.76\ \cancel{mol\,Cu} \times \frac{6.022 \times 10^{23} atoms\,Cu}{\cancel{mol\,Cu}} = 1.66 \times 10^{24} \text{molecules Cu}$$

Exercise 2.8.1

How many molecules are present in 4.61×10^{-2} mol of helium atoms?

Answer

2.78×10^{22} molecules

Converting between Mass and Number of Moles

The molar mass of a substance is defined as the mass in grams of 1 mole of that substance. One mole of isotopically pure carbon-12 has a mass of 12 g. For an element, the molar mass is the mass of 1 mol of atoms of that element. That is, the molar mass of a substance is the mass (in grams per mole) of 6.022×10^{23} atoms of that substance. In each case, the number of grams in 1 mol is the same as the number of atomic mass units that describe the atomic mass.

The periodic table lists the atomic mass of carbon as 12.011 amu; the average molar mass of carbon—the mass of 6.022×10^{23} carbon atoms—is therefore 12.011 g/mol.

Reminder: Molar Masses (Atomic Masses) are Weighted Averages of Isotopic Masses

As discussed in Section 1.9, The molar mass of naturally-occurring carbon is different from that of carbon-12 isotope because carbon occurs as a mixture of carbon-12, carbon-13, and carbon-14. One mole of carbon still has 6.022×10^{23} carbon atoms, but 98.89% of those atoms are carbon-12, 1.11% are carbon-13, and a trace (about 1 atom in 1012) are carbon-14. Similarly, the molar mass of uranium is 238.03 g/mol.

The mole is the basis of quantitative chemistry and provides chemists with a way to convert easily between the mass of a substance and the number of individual atoms, molecules, or formula units of that substance. Conversely, it enables chemists to calculate the mass of a substance needed to obtain a desired number of atoms. For example, to convert moles of a substance to mass, the following relationship is used:

$$(\text{moles}) \times (\text{molar mass}) \rightarrow \text{mass} \tag{2.8.3}$$

or, more specifically,

$$\cancel{\text{moles}} \times \left(\frac{\text{grams}}{\cancel{\text{mole}}}\right) = \text{grams}$$

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

$$\left(\frac{\text{grams}}{\text{molar mass}}\right) \rightarrow \text{moles} \tag{2.8.4}$$

$$\left(\frac{\text{grams}}{\text{grams/mole}}\right) = \cancel{\text{grams}} \left(\frac{\text{mole}}{\cancel{\text{grams}}}\right) = \text{moles} \tag{2.8.5}$$

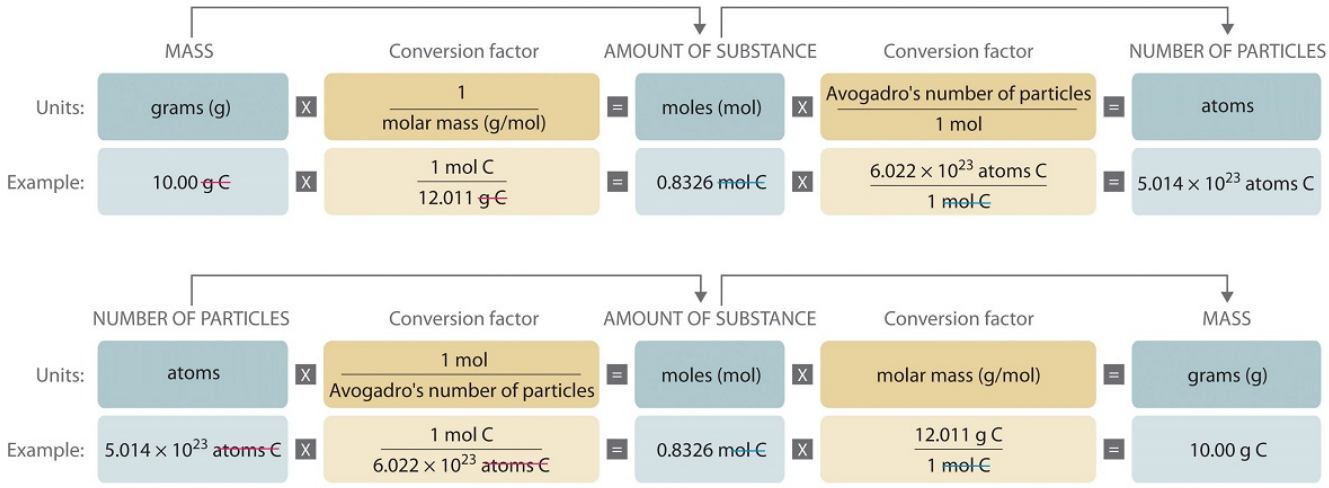


Figure 2.8.1: Forward and Reverse Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms. This is expanded version of Figure 2.8.3(CC BY-NC-SA 3.0; anonymous)

If know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

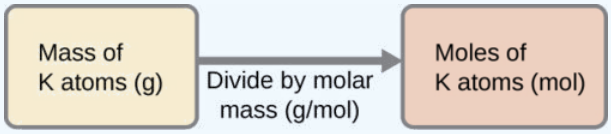
✔ Example 2.8.2: Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit "g" cancels and the answer has units of "mol:"

$$4.7 \cancel{\text{g}}\text{K}\left(\frac{\text{mol K}}{39.10 \cancel{\text{g}}}\right) = 0.12 \text{ mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

? Exercise 2.8.2: Beryllium

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

Answer

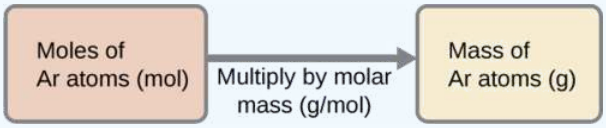
0.360 mol

Example 2.8.3: Deriving Grams from Moles for an Element

A liter of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a liter of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth (~10^{-3}) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4} \cancel{\text{mol}}\ \text{Ar} \left(\frac{39.95\ \text{g}}{\cancel{\text{mol}}\ \text{Ar}} \right) = 0.037\ \text{g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

Exercise 2.8.3

What is the mass of 2.561 mol of gold?

Answer

504.4 g

Example 2.8.4: Deriving Number of Atoms from Mass for an Element

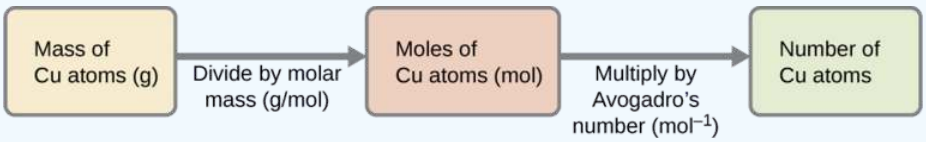
Copper is commonly used to fabricate electrical wire (Figure 2.8.6). How many copper atoms are in 5.00 g of copper wire?



Figure 2.8.6: Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu

atoms. Carrying out the two-step computation yields:

$$5.00 \cancel{g}\ \text{Cu} \left(\frac{\cancel{\text{mol}}\ \text{Cu}}{63.55 \cancel{g}} \right) \left(\frac{6.022 \times 10^{23}\ \text{atoms}}{\cancel{\text{mol}}} \right) = 4.74 \times 10^{22}\ \text{atoms of copper} \tag{2.8.6}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

? Exercise 2.8.4

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Answer

$4.586 \times 10^{22}\ Au$ atoms

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CHAPTER OVERVIEW

3: The Quantum-Mechanical Model of the Atom

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.

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3.1: Schrödinger's Cat

The field of chemistry deals with the structures, bonding, reactivity, and physical properties of atoms, molecules, radicals, and ions all of whose sizes range from ca. 1 Å for atoms and small molecules to a few hundred Å for polymers and biological molecules such as DNA and proteins. The description of the motions and properties of the particles comprising such small systems has been found to not be amenable to treatment using classical mechanics. Their structures, energies, and other properties have only been successfully described within the framework of quantum mechanics. This is why **quantum mechanics** has to be mastered as part of learning chemistry.

The concepts of quantum mechanics were invented to explain experimental observations that otherwise were totally inexplicable. This period of invention extended from 1900 when Max Planck introduced the revolutionary concept of quantization to 1925 when Erwin Schrödinger and Werner Heisenberg independently introduced two mathematically different but equivalent formulations of a general quantum mechanical theory. In the early 1930's Schrödinger published a way of thinking about the circumstance of radioactive decay that is still useful. We imagine an apparatus containing just one Nitrogen-13 atom and a detector that will respond when the atom decays. Connected to the detector is a relay connected to a hammer, and when the atom decays the relay releases the hammer which then falls on a glass vial containing poison gas. We take the entire apparatus and put it in a box. We also place a cat in the box, close the lid, and wait 10 minutes.

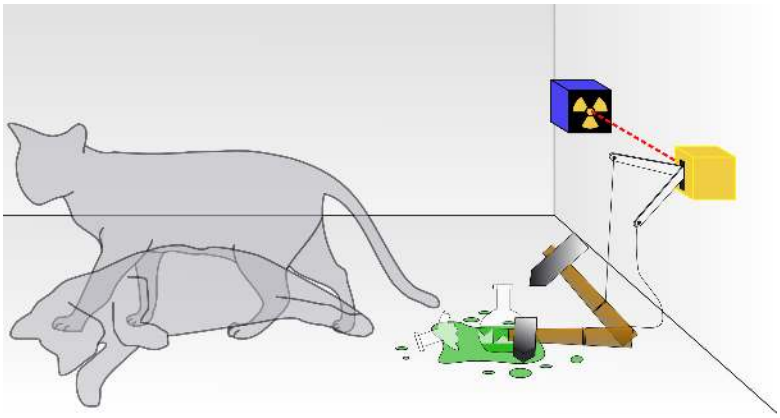


Figure 3.1.1: Schrödinger's cat: a cat, a flask of poison, and a radioactive source are placed in a sealed box. If an internal monitor detects radioactivity (i.e., a single atom decaying), the flask is shattered, releasing the poison, which kills the cat. The Copenhagen interpretation of quantum mechanics implies that after a while, the cat is simultaneously alive and dead. Yet, when one looks in the box, one sees the cat either alive or dead, not both alive and dead. This poses the question of when exactly quantum superposition ends and reality collapses into one possibility or the other. (CC BY-SA 3.0; Dhatfield).

We then ask: Is the cat alive or dead? The answer according to quantum mechanics is that it is 50% dead and 50% alive. Quantum mechanics often gives odd results from a classical perspective.

In this chapter, we will use quantum mechanismcs to 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.

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3.2: The Nature of Light

Learning Objectives

- Explain the basic behavior of waves, including traveling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Describe the particle nature of light

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.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.



Figure 3.2.1: 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. (CC BY-SA-NC; anonymous)

Waves Nature of Light

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 3.2.1). 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.

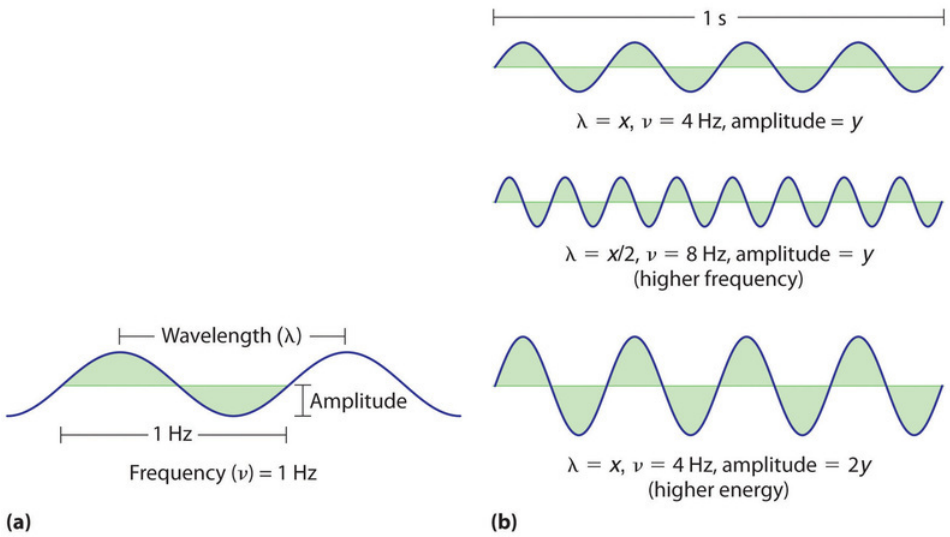


Figure 3.2.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy. (CC BY-SA-NC; anonymous)

Waves have characteristic properties (Figure 3.2.2). As you may have noticed in Figure 3.2.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the **wavelength** (λ, lowercase Greek lambda). Wavelengths are described by a unit of distance, typically meters. The **frequency** (ν, lowercase Greek nu) of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation.

The **amplitude**, or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 3.2.2, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(\text{wavelength})(\text{frequency}) = \text{speed}$$

$$\lambda\nu = v \tag{3.2.1}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{wave}}{\text{second}}\right) = \frac{\text{meters}}{\text{second}} \tag{3.2.2}$$

Different types of waves may have vastly different possible speeds and frequencies. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as **electromagnetic radiation**. (Figure 3.2.3). Some forms of electromagnetic radiation are shown in Figure 3.2.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which turns out to be a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

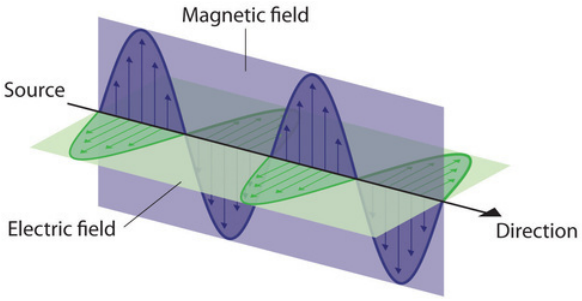


Figure 3.2.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields. (CC BY-SA-NC; anonymous)

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 3.2.4 and Table 3.2.1, 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 3.2.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda\nu \tag{3.2.3}$$

$$\nu = \frac{c}{\lambda} \tag{3.2.4}$$

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.

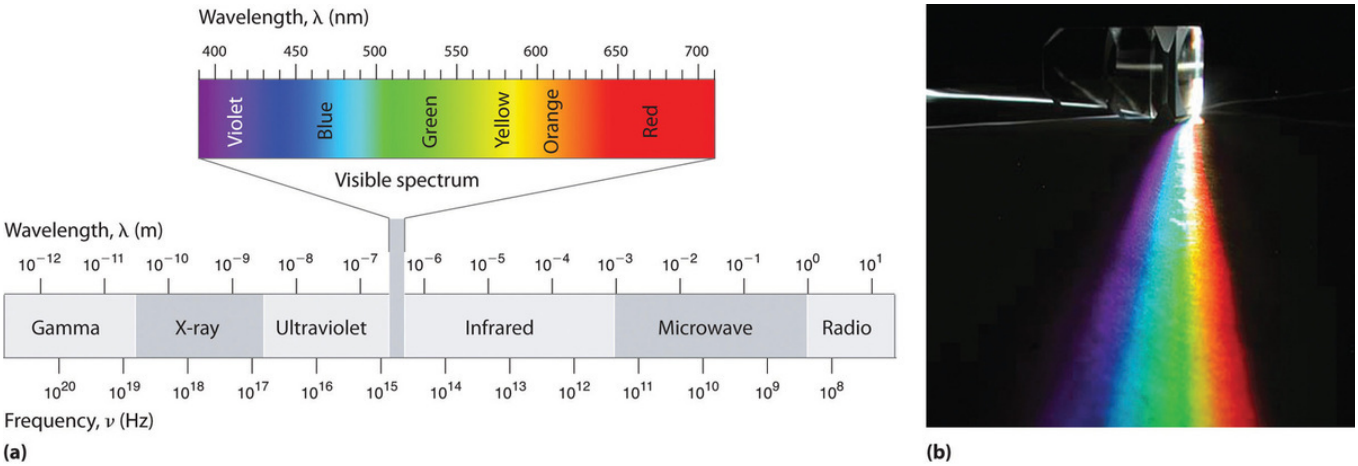


Figure 3.2.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum. (CC BY-SA-NC; anonymous)

Within the visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism (Figure 3.2.4a). A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 3.2.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	UV, visible
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu \tag{3.2.5}$$

$$\propto \frac{1}{\lambda} \tag{3.2.6}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer of the atmosphere absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

> *The energy of electromagnetic radiation increases with increasing frequency and decreasing wavelength.*

Example 3.2.1: Wavelength of Radiowaves

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 3.2.4 to calculate the wavelength in meters.

Solution:

From Equation 3.2.4, 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:

$$\lambda\nu = c$$
$$= 2.998 \times 10^8 m/s$$

Thus the wavelength λ is given by

$$\lambda = \frac{c}{\nu}$$
$$= \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \cancel{MHz}}\right)\left(\frac{1\ \cancel{MHz}}{10^6\ \cancel{s^{-1}}}\right)$$
$$= 2.965\ m$$

? Exercise 3.2.1

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

Interference and Diffraction

When two or more waves arrive at the same point, they superimpose themselves on one another. More specifically, the disturbances of waves are superimposed when they come together—a phenomenon called **superposition**. Each disturbance corresponds to a force, and forces add. If the disturbances are along the same line, then the resulting wave is a simple addition of the disturbances of the individual waves—that is, their amplitudes add. Figures 3.2.5 and 3.2.6 illustrate superposition in two special cases, both of which produce simple results.

Figure 3.2.5 shows two identical waves that arrive at the same point exactly in phase. The crests of the two waves are precisely aligned, as are the troughs. This superposition produces pure **constructive interference**. Because the disturbances add, pure constructive interference produces a wave that has twice the amplitude of the individual waves, but has the same wavelength.

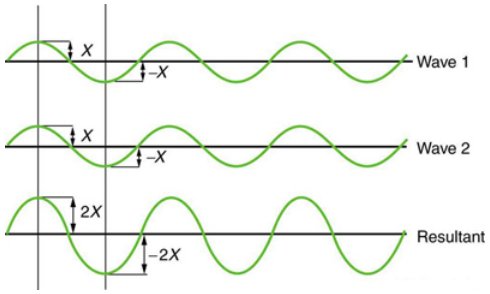


Figure 3.2.5: Pure constructive interference of two identical waves produces one with twice the amplitude, but the same wavelength. (CC BY 4.0; OpenStax)

Figure 3.2.6 shows two identical waves that arrive exactly out of phase—that is, precisely aligned crest to trough—producing pure **destructive interference**. Because the disturbances are in the opposite direction for this superposition, the resulting amplitude is zero for pure destructive interference—the waves completely cancel.

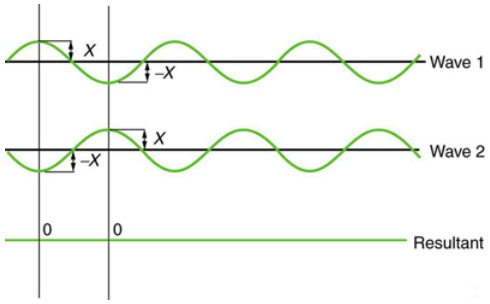


Figure 3.2.6: Pure destructive interference of two identical waves produces zero amplitude, or complete cancellation. (CC BY 4.0; OpenStax)

While pure constructive and pure destructive interference do occur, they require precisely aligned identical waves. The superposition of most waves produces a combination of constructive and destructive interference and can vary from place to place and time to time. Sound from a stereo, for example, can be loud in one spot and quiet in another. Varying loudness means the sound waves add partially constructively and partially destructively at different locations. A stereo has at least two speakers creating sound waves, and waves can reflect from walls. All these waves superimpose. An example of sounds that vary over time from constructive to destructive is found in the combined whine of airplane jets heard by a stationary passenger. The combined sound can fluctuate up and down in volume as the sound from the two engines varies in time from constructive to destructive.

The Particle Nature of Light

When certain metals are exposed to light, electrons are ejected from their surface (Figure 3.2.7). 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).

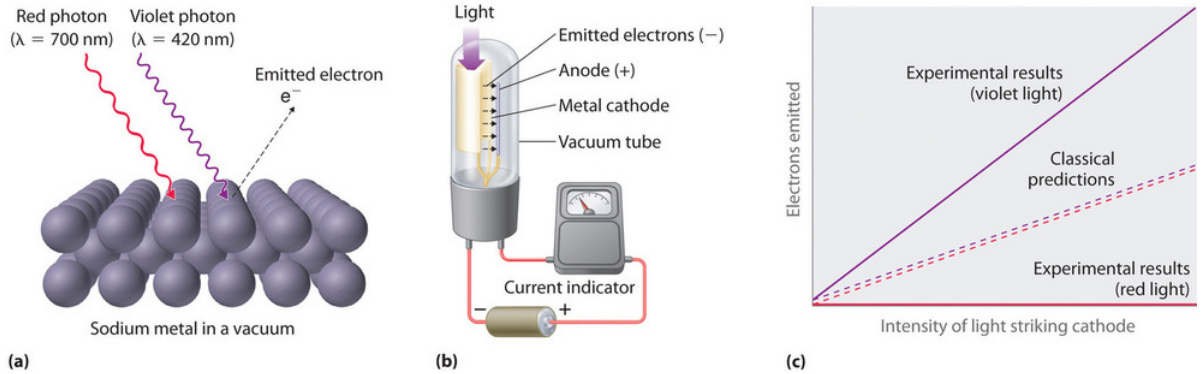


Figure 3.2.7: The Photoelectric Effect (a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons 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.

In 1900, the German physicist Max Planck (1858–1947) proposing that the energy of electromagnetic waves is *quantized* rather than continuous. Planck postulated that the energy of a particular quantum of radiant energy could be described by the equation

$$E = hu \tag{3.2.7}$$

where the proportionality constant *h* is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34}\, J \cdot s \,(\text{joule-seconds})$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. 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.

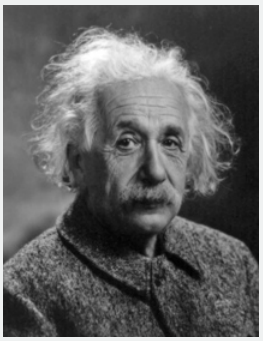
Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant energy arrives at the metal surface in particles that we now call **photons** (a quantum of radiant energy, each of which possesses a particular energy energy E given by Equation 3.2.7 Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = u_o$). If photons of light with energy less than E_o strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than E_o strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron:

$$\begin{aligned} \text{kinetic energy of ejected electron} &= E - E_o \\ &= h\nu - h\nu_o \\ &= h\,(\nu - \nu_o) \end{aligned} \tag{3.2.8}$$

When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the *number* of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics. Moreover, the idea that light could behave not only as a wave but as a particle in the form of photons suggested that matter and energy might not be such unrelated phenomena after all.

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 3.2.2

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 3.2.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A. Use Equation 3.2.7 and the relationship between wavelength and frequency to calculate the energy in joules.

Solution:

The energy of a single photon is given by

$$E = h\nu = \frac{hc}{\lambda}. \tag{3.2.9}$$

Exercise 3.2.2

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

$1.287 \times 10^{-15}\ J/photon$

Answer a

4497 times

Example 3.2.3: Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
c. True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.
d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

Exercise 3.2.3

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is $9.87 \times 10^{14}\ Hz$.

Answer

$3.94\ kJ/mol$

Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of 2.998×10^8 m s^{-1}. This radiation shows wavelike behavior, which can be characterized by a frequency, ν, and a wavelength, λ, such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$ (or $E = \frac{hc}{\lambda}$), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it.

Key Equations

- $c = \lambda\nu$
- $E = h\nu = \frac{hc}{\lambda}$, where $h = 6.626 \times 10^{-34}$ J s

Summary

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A **wave** is a periodic oscillation by which energy is transmitted through space. All waves are **periodic**, repeating regularly in both space and time. Waves are characterized by several interrelated properties: **wavelength** (λ), the distance between successive waves; **frequency** (u), the number of waves that pass a fixed point per unit time; **speed** (v), the rate at which the wave propagates through space; and **amplitude**, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. **Electromagnetic radiation** consists of two perpendicular waves, one electric and one magnetic, propagating at the **speed of light** (c). Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

Glossary

amplitude
: extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

continuous spectrum
: electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

electromagnetic radiation
: energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum
: range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

frequency (ν)
: number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

hertz (Hz)
: the unit of frequency, which is the number of cycles per second, s^{-1}

intensity
: property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern
: pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

line spectrum
: electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

node
: any point of a standing wave with zero amplitude

photon
: smallest possible packet of electromagnetic radiation, a particle of light

quantization

occurring only in specific discrete values, not continuous

standing wave

(also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

wave

oscillation that can transport energy from one point to another in space

wavelength (λ)

distance between two consecutive peaks or troughs in a wave

wave-particle duality

term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

Contributors and Attributions

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3.3: Atomic Spectroscopy and The Bohr Model

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

The concept of the photon emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. However, more direct evidence was needed to verify the quantized nature of energy in all matter. In this section, we describe how observation of the interaction of atoms with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation, a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a **line spectrum**, are observed rather than a continuous range of wavelengths (Figure 3.3.1). The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

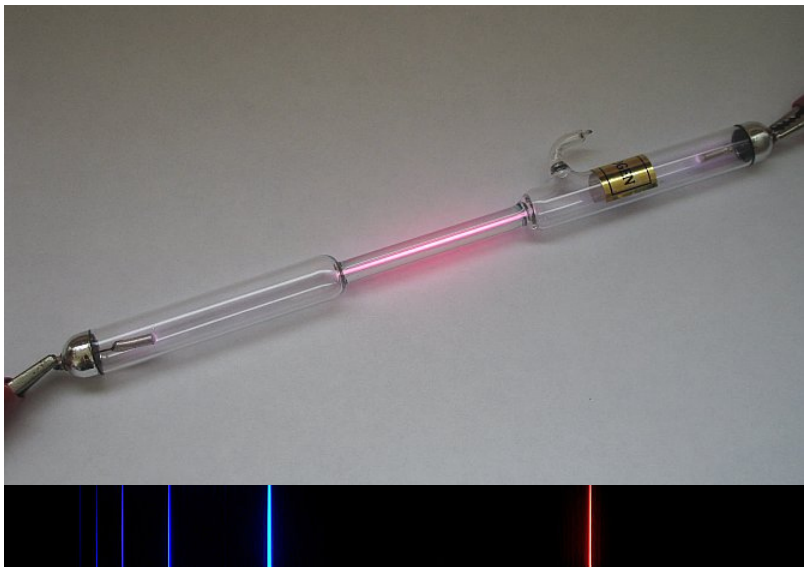


Figure 3.3.1: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (CC BY-SA 3.0 Unported; Science Made Alive via Wikipedia) (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm. (CC BY-SA 3.0; Jan Homann via Wikipedia)

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation: the observation of only a few values of λ (or u) in the line spectrum meant that only a few values of E were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

$$u = constant\ \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{3.3.1}$$

where n = 3, 4, 5, 6. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

$$\frac{1}{\lambda} = \Re\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{3.3.2}$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\Re$ the *Rydberg constant*, has a value of 1.09737 × 10^7 m^{-1}.

Johann Balmer (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous.



Balmer published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with n_1 = 2, n_2 = 3, 4, 5,…). More important, Rydberg's equation also predicted the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet (n_1 = 1, n_2 = 2, 3, 4,…) and one in the infrared (n_1 = 3, n_2 = 4, 5, 6). Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

Bohr's Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii*. Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.

Using classical physics, Niels Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\Re hc}{n^2} \tag{3.3.3}$$

where $\Re$ is the Rydberg constant, h is Planck's constant, c is the speed of light, and n is a positive integer corresponding to the number assigned to the orbit, with n = 1 corresponding to the orbit closest to the nucleus. In this model $n = \infty$ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.

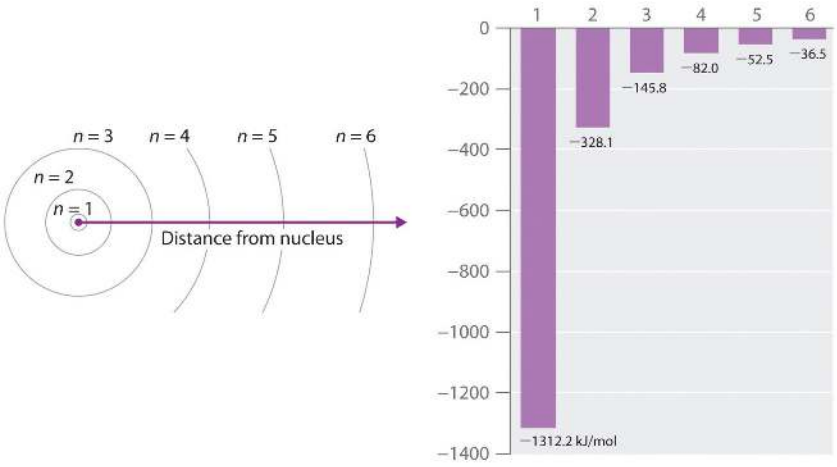
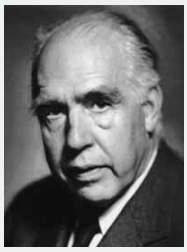


Figure 3.3.2: The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing *n*. (b) The energy of the orbit becomes increasingly less negative with increasing *n*.

Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project.



In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative sign in Equation 3.3.3 indicates that the electron-nucleus pair is more tightly bound (i.e. at a lower potential energy) when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the **ground state** (the most stable arrangement of electrons for an element or a compound) for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure 3.3.2*a*). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the *difference* in energy between the two states (Figure 3.3.1).

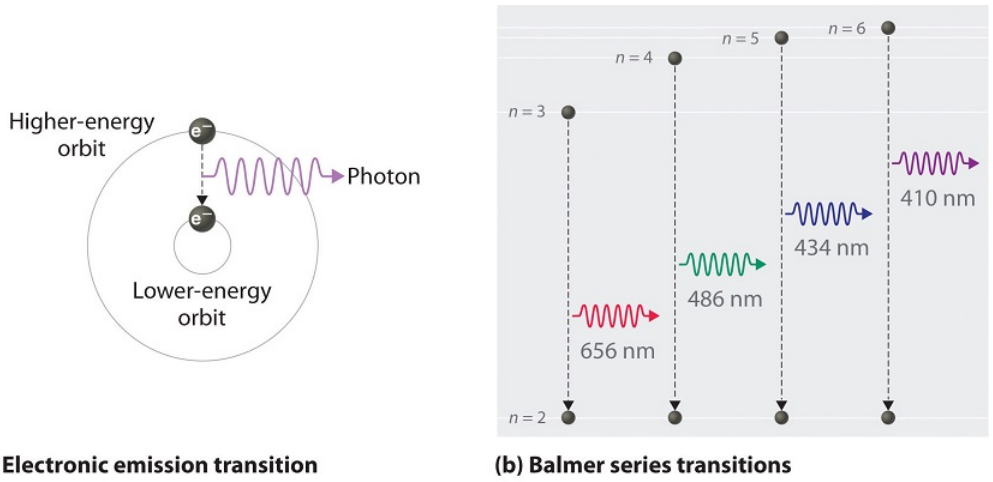


Figure 3.3.3: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of *n* (at a higher energy) to an orbit with a lower value of *n* (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with $n \geq 3$ to the orbit with $n = 2$. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_1} - E_{n_2}$ where n_1 is the final orbit and n_2 the initial orbit. Substituting from Bohr's equation (Equation 3.3.3) for each energy value gives

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= -\frac{\Re hc}{n_2^2} - \left(-\frac{\Re hc}{n_1^2}\right) \\ &= -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)\end{aligned}$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure 3.3.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{3.3.4}$$

Canceling hc on both sides gives

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{3.3.5}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 3.3.4 and 3.3.5 indicates that energy is released as the electron moves from orbit n_2 to orbit n_1 because orbit n_2 is at a higher energy than orbit n_1. Bohr calculated the value of $\Re$ from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of $1.0974 \times 10^7\ m^{-1}$, 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 (3.3.3*b*); the lines in this series correspond to transitions from higher-energy orbits (n > 2) to the second orbit (n = 2). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state (n > 2) to a lower-energy state (n = 2) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the difference in energy between the two states (Figure 3.3.3*a*). The n = 3 to n = 2 transition gives rise to the line at 656 nm (red), the n = 4 to n = 2 transition to the line at 486 nm (green), the n = 5 to n = 2 transition to the line at 434 nm (blue), and the n = 6 to n = 2 transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the n = 3 than the n ≥ 4 levels. Consequently, the n = 3 to n = 2 transition is the most intense line, producing the characteristic

red color of a hydrogen discharge (Figure 3.3.1*a*). Other families of lines are produced by transitions from excited states with n > 1 to the orbit with n = 1 or to orbits with n ≥ 3. These transitions are shown schematically in Figure 3.3.4

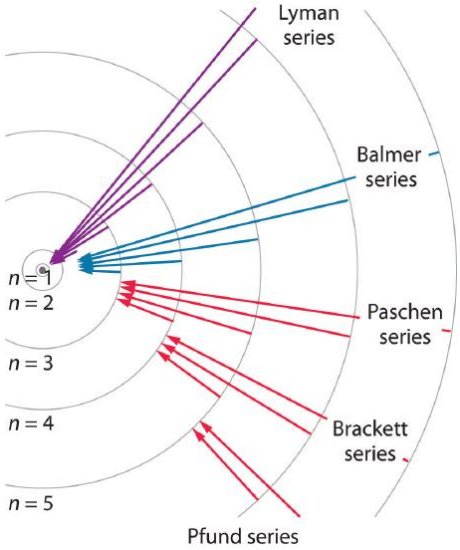


Figure 3.3.4: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

Using Atoms to Time

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis.

To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum.

In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

Example 3.3.1: The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the n = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A. Substitute the appropriate values into Equation 3.3.2 (the Rydberg equation) and solve for λ.
B. Use Figure 2.2.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

A For the Lyman series, n_1 = 1. The lowest-energy line is due to a transition from the n = 2 to n = 1 orbit because they are the closest in energy.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1}$$

It turns out that spectroscopists (the people who study spectroscopy) use cm^{-1} rather than m^{-1} as a common unit. Wavelength is inversely proportional to energy but frequency is directly proportional as shown by Planck's formula, $E = hu$.

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 200 - 5,000 cm^{-1}, the visible from 11,000 to 25.000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1}. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1}.

$$\tilde{u} = \frac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m}^{-1}\left(\frac{\cancel{m}}{100\ cm}\right) = 82,280\ cm^{-1}$$

and

$$\lambda = 1.215 \times 10^{-7}\ m = 122\ nm$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets, producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone.

B This wavelength is in the ultraviolet region of the spectrum.

? Exercise 3.3.1: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the n = 5 orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer

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:

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 3.3.5). In fact, Bohr's model worked only for species that contained just one electron: H, He^+, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

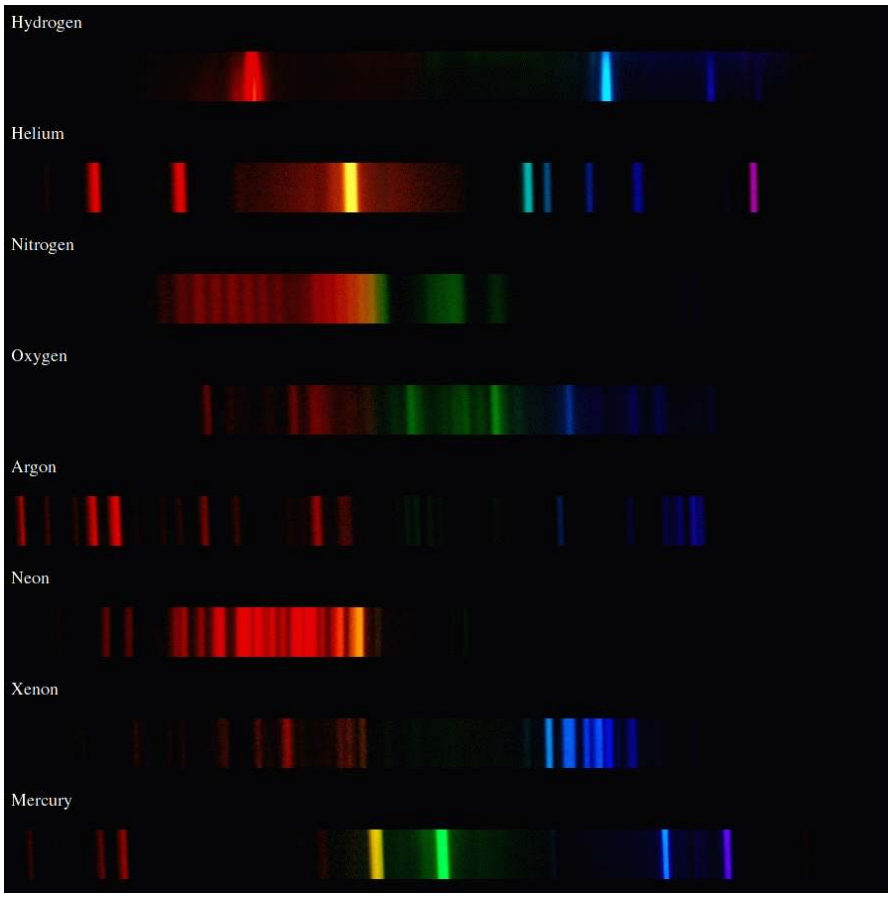


Figure 3.3.5: The atomic emission spectra for various elements. Each thin band in each spectrum corresponds to a single, unique transition between energy levels in an atom. Image from the Rochester Institute of Technology, CC BY-NC-SA 2.0.

Atomic Spectroscopy and the Identification of Elements

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum (a spectrum produced by the emission of light by atoms in excited states). The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum (a spectrum produced by the absorption of light by ground-state atoms).

> When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.

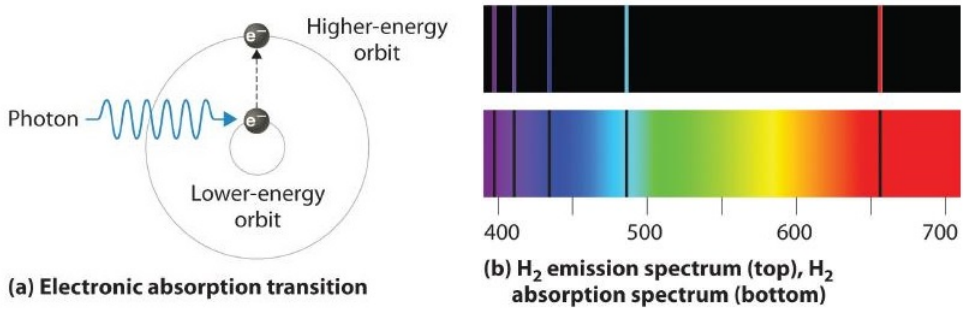


Figure 3.3.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here. (CC BY-NC-SA 3.0; anonymous)

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 3.3.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning “sun.” Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium pick up electrons from the rocks to form helium atoms.

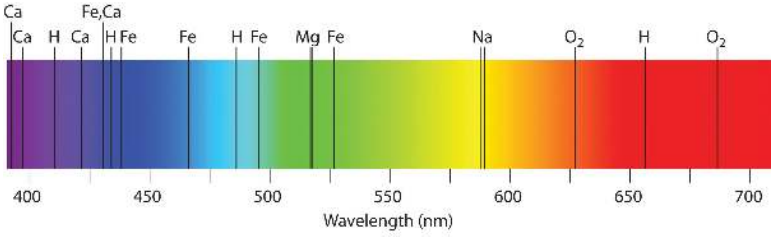


Figure 3.3.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun’s atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth’s atmosphere. (CC BY-NC-SA 3.0; anonymous)

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 3.3.5. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 3.3.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

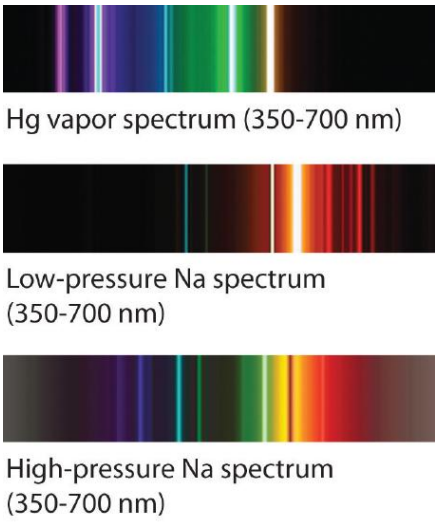


Figure 3.3.8: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp. (CC BY-NC-SA 3.0; anonymous)

Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

Key Concepts

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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3.4: The Wavelength Nature of Matter

Learning Objectives

- To understand the wave–particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. Light exhibits a **wave-particle duality** and may described as either a particle or a wave depending on the experiment.

Diffraction is a Wave Phenomenon

It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of light diffraction is the Young double slit experiment (Figure 3.4.1).



Figure 3.4.1: Young double slit experiment demonstrate the wave behavior of light. Two slits are illuminated by a plane light waves. (CC BY-NC; Thomas Widerman)

Here, we use light pictured as waves in a plane parallel to the double slit apparatus and observe what happens when they impinge on the slits. Each slit becomes a point source for spherical waves that subsequently interfere with each other, giving rise to the light and dark fringes on the screen at the right. Interference is a wave phenomenon in which two *waves* superimpose to form a resultant wave of greater or lower amplitude. It is a primary property used to identify wave behavior in nature.

According to classical physics, electrons should behave like particles - they travel in straight lines and do not curve in flight unless acted on by an external agent, like a magnetic field. In this model, if we fire a beam of electrons through a double slit onto a detector, we should get two bands of "hits", much as you would get if you fired a machine gun at the side of a house with two windows - you would get two areas of bullet-marked wall inside, and the rest would be intact Figure 3.4.2;. However, if the slits are made small enough and close enough together, experimentalist actually observe the electrons *diffracting* through the slits and *interfering* with each other just like light waves (Figure 3.4.2;). This means that the electrons exhibit a similar wave-particle duality

that light exhibits. In this case, they must have properties like wavelength and frequency. We can deduce the properties from the behavior of the electrons as they pass through our diffraction grating.

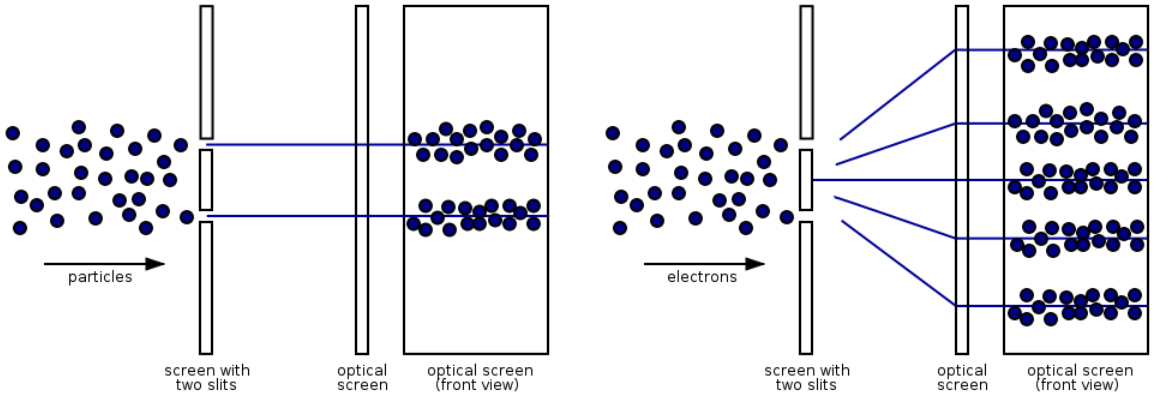


Figure 3.4.2: (left) classical model of electrons. (right) wave property of electrons.

The observation that particles may exhibit wavelength phenomena was a pivotal result in the development of quantum mechanics. For physicists this idea was important because it meant that not only could any particle exhibit wave characteristics, but that one could use wave equations to describe phenomena in matter. In his PhD dissertation submitted to the Sorbonne in 1924, Louis de Broglie (1892–1972) proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{mv} \tag{3.4.1}$$

where

- λ is the de Broglie wavelength,
- h is Planck's constant,
- m is the mass of the particle, and
- v is the velocity of the particle.

It turned out that de Broglie hypothesis was able to accurately describe a range of diffraction phenomena of matter. 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 (Equation 3.4.1, which is an extremely small number. As you will calculate in Example 3.4.1, Planck's constant (6.63×10^{-34} J•s) is so small that the wavelength of a particle with a large mass is simply too short (less than the diameter of an atomic nucleus) to be noticeable.

Example 3.4.1: Wavelength of a Baseball in Motion

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.
B. Substitute values into Equation 3.4.1 and solve for the wavelength.

Solution:

The wavelength of a particle is given by $\lambda = h/mv$. We know that m = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)$$

B Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)}$$

$$= \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}\,\cancel{^{-2}} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s^{-1}}\right)}$$

$$= 9.95 \times 10^{-35}\ m$$

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

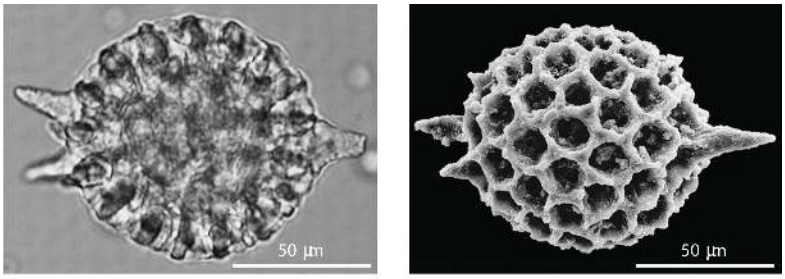
? Exercise 3.4.1: Wavelength of a Neutron in Motion

Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer

1.32 Å, or 132 pm

As you calculated in Example 3.4.1, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, however, such as electrons, exhibit the properties of both particles *and* waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 3.4.3).



(a) Radiolarian under light microscope (b) Radiolarian under electron microscope

Figure 3.4.3: 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.)

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. Hence, an "uncertainty principle" for light is merely a conclusion about the nature of electromagnetic waves and nothing new. De Broglie's idea of wave-particle duality means that particles such as electrons which exhibit an uncertainty principle. This was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that “at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation.” Mathematically, the **Heisenberg uncertainty principle** states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck’s constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geq \frac{h}{4\pi} \tag{3.4.2}$$

Because Planck's constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie's equation to have measurable wavelengths.

If the precise position x of a particle is known absolutely ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

$$(\Delta [mv]) = \frac{h}{4\pi (\Delta x)} = \frac{h}{4\pi (0)} = \infty \tag{3.4.3}$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 3.4.3, 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.

Example 3.4.2: The Uncertainty Principle Large and Small

Determine the minimum uncertainties in the positions of the following objects if their speeds are known with a precision of $1.0 \times 10^{-3} m/s$:

1. an electron and
2. a bowling ball of mass 6.0 kg.

Strategy

Given the uncertainty in speed $\Delta u = 1.0 \times 10^{-3} m/s$, we have to first determine the uncertainty in momentum $\Delta p = m\Delta u$ and then invert Equation ??? to find the uncertainty in position

$$\Delta x = \frac{\hbar}{2\Delta p}.$$

Solution

1. For the electron:

$$\begin{aligned} \Delta p &= m\Delta u \\ &= (9.1 \times 10^{-31} kg)(1.0 \times 10^{-3} m/s) \\ &= 9.1 \times 10^{-34} kg \cdot m/s, \end{aligned}$$

$$\begin{aligned} \Delta x &= \frac{\hbar}{2\Delta p} \\ &= 5.8\, cm. \end{aligned}$$

2. For the bowling ball:

$$\begin{aligned} \Delta p &= m\Delta u \\ &= (6.0\, kg)(1.0 \times 10^{-3} m/s) \\ &= 6.0 \times 10^{-3} kg \cdot m/s, \end{aligned}$$

$$\begin{aligned} \Delta x &= \frac{\hbar}{2\Delta p} \\ &= 8.8 \times 10^{-33} m. \end{aligned}$$

Significance

Unlike the position uncertainty for the electron, the position uncertainty for the bowling ball is immeasurably small. Planck's constant is very small, so the limitations imposed by the uncertainty principle are not noticeable in macroscopic systems such as a bowling ball.

Indeterminacy and Probability Distribution Maps

Before either quantum mechanics, physicists described the world using "Classical Mechanics," which is like what you've probably studied before in physics class: Newtonian mechanics (forces, accelerations, etc), electricity and magnetism using Maxwell's equations. All these approaches work well for big things that are not moving too fast. There are two qualities of classical mechanics that quantum mechanics altered. First, in classical mechanics energy and velocity and such quantities can have any value. If you drop a ball, it accelerates smoothly from 0 to a final velocity, rather than moving jerkily from step to step. The Quantum Mechanics got rid of the assumptions that energy and velocity should be "continuous."

A **trajectory** is the path that an object with mass in motion follows through space as a function of time. In classical mechanics, a complete trajectory is defined by knowledge of *position* and *momentum*, simultaneously. If you launch a missile, a space shuttle or kick a ball (Figure 3.4.1), you can calculate almost exactly the path it will follow; if you have *perfect* knowledge of the forces acting on it, you can calculate its path *perfectly*. This is because Newton's laws are completely **deterministic** - that is because they imply that anything that happens at any future time is completed determined by what happens now, and moreover that everything now was completely determined by what happened at any time in the past.

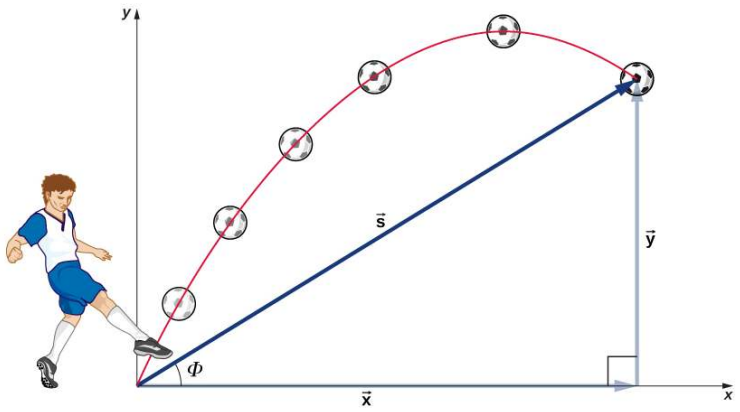


Figure 3.4.1: The total displacement s of a soccer ball at a point along its path. The vector $\vec{s}$ has components $\vec{x}$ and $\vec{y}$ along the horizontal and vertical axes. Its magnitude is s and it makes an angle ϕ with the horizontal. (CC BY 4.0; Openstax)

However, as discussed above, due to Heisenberg uncertainty principle, position and momentum cannot be measured simultaneously. This means the concept of a trajectory in quantum mechanics is not defined and we actually do not know where they are or what path they follow (Figure 3.4.4). Quantum mechanics is a **probabilitic** theory, that discards the concept of trajectory for small particles, and uses statistics and probability to describe evolution.

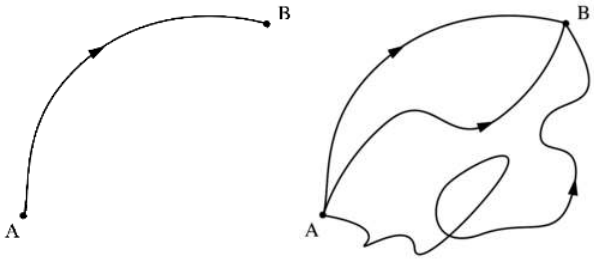


Figure 3.4.4: (left) Classical trajectory of a particle evolving from point A to point B. (right) The quantum analog. These are just three of the infinitely many paths that contribute to the quantum amplitude for a particle moving from point A at some time t_0 to point B at some other time t_1. (CC BY-SA 2.5; Matt McIrvin)

Summary

An electron possesses both particle and wave properties. The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle.

$$\lambda = \frac{h}{mv}$$

The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi}$$

Contributors and Attributions

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3.5: Quantum Mechanics and The Atom

Learning Objectives

- To apply the results of quantum mechanics to electrons in atoms

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.

Schrödinger started with the simple requirement that the total energy of the electron is the sum of its kinetic and potential energies:

$$E = \underbrace{\frac{mv^2}{2}}_{\text{kinetic energy}} + \underbrace{\frac{-e^2}{r}}_{\text{potential energy}} \tag{3.5.1}$$

The second term represents the potential energy of an electron (whose charge is denoted by *e*) at a distance *r* from a proton (the nucleus of the hydrogen atom). In quantum mechanics it is generally easier to deal with equations that use momentum ($p = mv$) rather than velocity, so the next step is to make this substitution:

$$E = \frac{p^2}{2m} - \frac{e^2}{r} \tag{3.5.2}$$

This is still an entirely classical relation, as valid for the waves on a guitar string as for those of the electron in a hydrogen atom. The third step takes into account the wavelike character of the electron in the atom, a mathematical expression that describes the position and momentum of the electron at all points in space is applied to both sides of the equation. The function, denoted by ψ, "modulates" the equation of motion of the electron so as to reflect the fact that the electron manifests itself with greater probability in some locations that at others. This yields the celebrated **Schrödinger equation**

$$\left(\frac{mv^2}{2} - \frac{e^2}{r}\right)\psi = E\psi \tag{3.5.3}$$

which is often written as

$$H\psi = E\psi \tag{3.5.4}$$

where H is the **Hamiltonian** operator, E is the total energy of the electron, and ψ is the **wavefunction** of the electron. The Hamiltonian is a combination of operations that are used to extract the total energy of the system (e.g., the sum of kinetic an potential energies) and the wavefunction is a mathematical description of the quantum state of an isolated quantum system. The wavefunction is a complex-valued probability amplitude, and the probabilities for the possible results of measurements made on the system can be derived from it. Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Solutions to the Schrödinger Equation for the Hydrogen Atom

A wavefunction is a mathematical function that relates the location of an electron at a given point in space (identified by *x*, *y*, and *z* coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wavefunction is associated with a particular

energy E. The properties of wavefunctions derived from quantum mechanics are summarized here:

A wavefunction uses three variables to describe the position of an electron. A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates *x*, *y*, and *z*), and one specifies the time at which the object is at the specified location. For 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.

The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wave at that point. Many wavefunctions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$, represented as i. Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wavefunction (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wavefunction should *not* be confused with a positive or negative electrical charge.

The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space. The square of the wavefunction (ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] and is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wavefunction Ψ and its complex conjugate Ψ*, in which all terms that contain *i* are replaced by $-i$. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 3.5.2.

Describing the electron distribution as a standing wave leads to sets of *quantum numbers* that are characteristic of each wavefunction. From the patterns of one- and two-dimensional standing waves shown previously, you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wavefunctions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wavefunctions), each of which is specified by a set of numbers called quantum numbers.

Each wavefunction is associated with a particular energy. As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

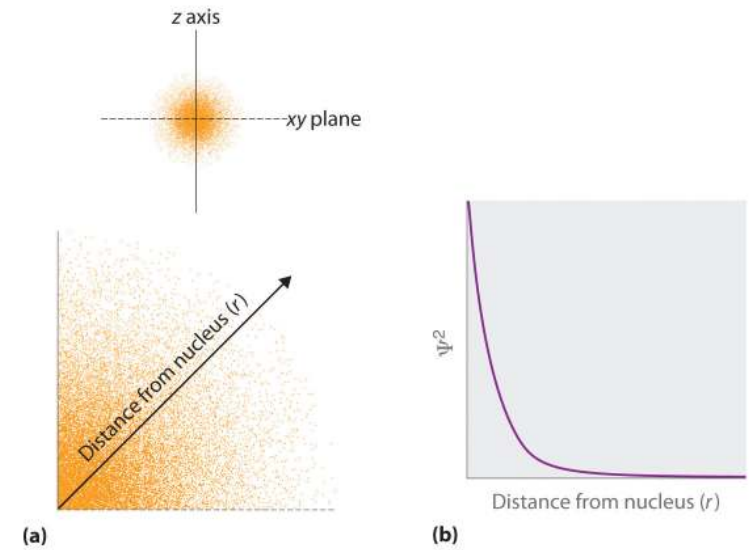


Figure 3.5.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but *not* zero.

Schrödinger's approach uses three quantum numbers (n, l, and m_l) to specify any wavefunction. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer, only certain values of l and m_l are allowed for a given value of n.

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \ldots \tag{3.5.5}$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wavefunctions that have the same value of n are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the **azimuthal quantum number (l)**. The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to $n - 1$:

$$l = 0, 1, 2, \ldots, n - 1 \tag{3.5.6}$$

For example, if $n = 1$, l can be only 0; if $n = 2$, l can be 0 or 1; and so forth. For a given atom, all wavefunctions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

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:

$$m_l = -l, -l + 1, \ldots, 0, \ldots, l - 1, l \tag{3.5.7}$$

For example, if $l = 0$, m_l can be only 0; if $l = 1$, m_l can be −1, 0, or +1; and if $l = 2$, m_l can be −2, −1, 0, +1, or +2.

Each wavefunction with an allowed combination of n, l, and m_l values describes an atomic **orbital**, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

The Spin Quantum Number

Example 3.5.1: n=4 Shell Structure

How many subshells and orbitals are contained within the principal shell with $n = 4$?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given $n = 4$, calculate the allowed values of l. From these allowed values, count the number of subshells.
B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n − 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to $n^2 = 16$

Exercise 3.5.1: 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 historical terms for corresponding spectroscopic characteristics: sharp, *p*rinciple, *d*iffuse, and *f*undamental.) A 1*s* orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = −1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = −2$, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.5.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1*s*); for $n = 2$, there are two subshells (2*s* and 2*p*); for $n = 3$, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2*d* subshell does not exist.

- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

> *Each principal shell has n subshells, and each subshell has 2l + 1 orbitals.*

Table 3.5.1: Values of n, l, and ml through n = 4

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

Summary

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wavefunctions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wavefunctions have five important properties:

1. the wavefunction uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron;
2. the magnitude of the wavefunction is proportional to the intensity of the wave;
3. the probability of finding an electron at a given point is proportional to the square of the wavefunction at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
4. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wavefunction; and
5. each spatial distribution of the electron described by a wavefunction with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** n can be any positive integer; as n increases for an atom, the average distance of the electron from the nucleus also increases. All wavefunctions with the same value of n constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** l can have integral values between 0 and $n − 1$; it describes the shape of the electron distribution. wavefunctions that have the same values of both n and l constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l + 1$ integral values, ranging from $−l$ to $+l$, and describes the orientation of the electron distribution. Each wavefunction with a given set of values of n, l, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

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3.6: The Shape of Atomic Orbitals

Learning Objectives

- To understand the 3D representation of electronic orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different **probabilities** of containing an electron.

One way of representing electron probability distributions was illustrated previously for the 1**s** orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (**r**) is a plot of the **probability density**. The 1**s** orbital is spherically symmetrical, so the probability of finding a 1**s** electron at any given point depends **only** on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of **r**, the electron probability density is very small but **not** zero.

In contrast, we can calculate the **radial probability** (the probability of finding a 1s electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of **x** spherical shells of radius $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$,…, $\mathbf{r}_{x-1}$, $\mathbf{r}_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (Figure 3.6.1*a*), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at r = 0 (Figure 3.6.1*b*), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 3.6.1. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (Figure 3.6.1*c*). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (Figure 3.6.1*d*). Most important, when r is very small, the surface area of a spherical shell is so small that the **total** probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure 3.6.1*d*).

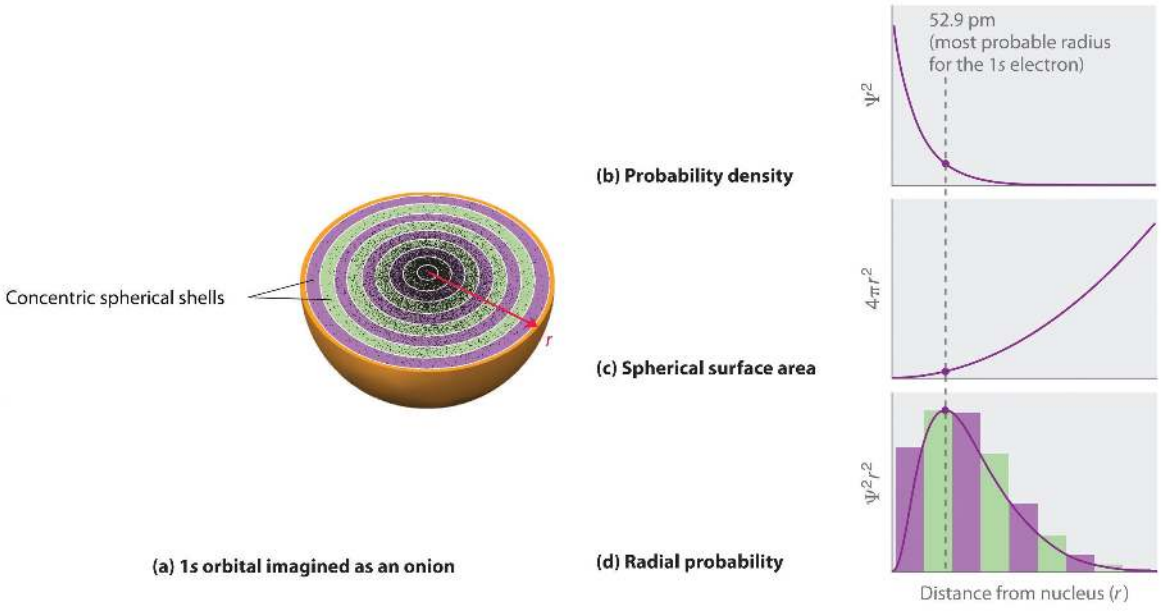


Figure 3.6.1: Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi\mathbf{r}^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the **radial probability**) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at r = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the **n** = 1 orbit. Thus the **most probable radius** obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 3.6.2 compares the electron probability densities for the hydrogen 1**s**, 2**s**, and 3**s** orbitals. Note that all three are spherically symmetrical. For the 2**s** and 3**s** orbitals, however (and for all other **s** orbitals as well), the electron probability density does not fall off smoothly with increasing r. Instead, a series of minima and maxima are observed in the radial probability plots (Figure 3.6.2*c*). The minima correspond to spherical **nodes** (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave **phase** in the wavefunction Ψ.

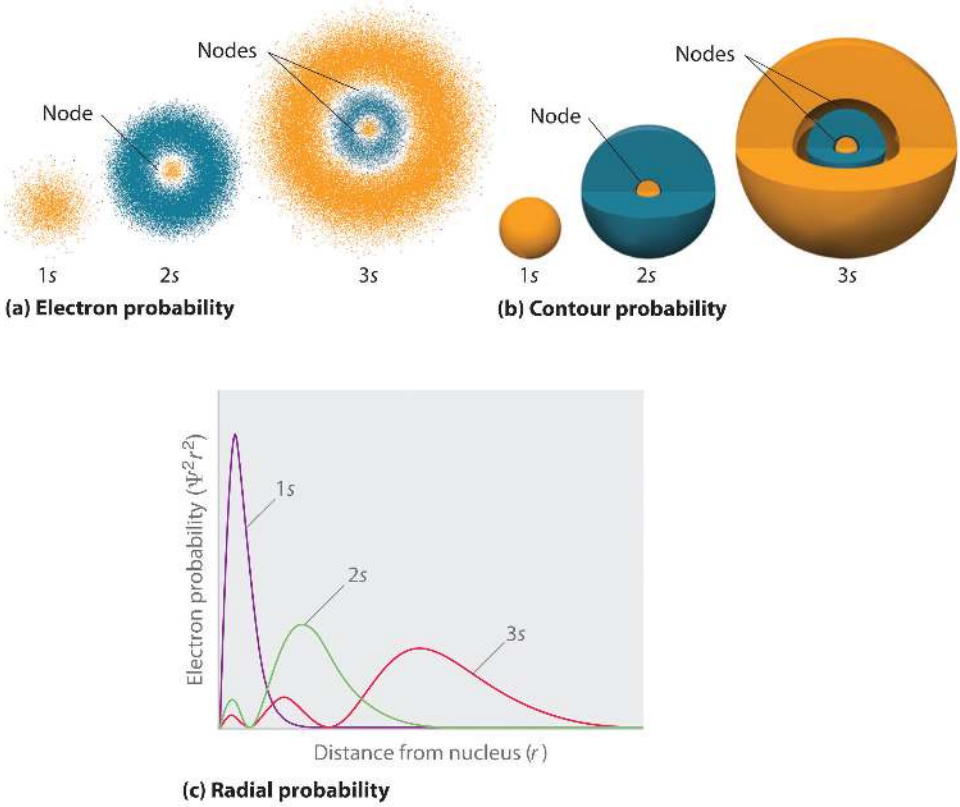


Figure 3.6.2: Probability Densities for the 1**s**, 2**s**, and 3**s** Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1**s**, 2**s**, and 3**s** orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (**r**) in all directions (radial probability), the most probable radius increases as **n** increases, but the 2**s** and 3**s** orbitals have regions of significant electron probability at small values of r.

s Orbitals (l=0)

Three things happen to **s** orbitals as **n** increases (Figure 3.6.2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the **s** orbitals also become higher in energy as **n** increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1**s**, 2**s**, and 3**s** orbitals in part (b) in Figure 3.6.2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2**s** and 3**s** orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only **s** orbitals are spherically symmetrical. As the value of **l** increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2**p** subshell has **l** = 1, with three values of $\mathbf{m_l}$ (−1, 0, and +1), there are three 2**p** orbitals.

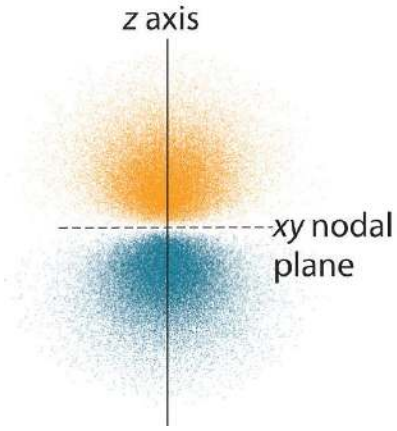


Figure 3.6.3: Electron Probability Distribution for a Hydrogen 2**p** Orbital. The nodal plane of zero electron density separates the two lobes of the 2**p** orbital. As in Figure 3.6.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2**p** orbitals is shown in Figure 3.6.3. Because this orbital has two lobes of electron density arranged along the **z** axis, with an electron density of zero in the **xy** plane (i.e., the **xy** plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 3.6.4, the other two 2**p** orbitals have identical shapes, but they lie along the **x** axis ($2p_x$) and y axis ($2p_y$), respectively. Note that each **p** orbital has just one **nodal plane**. In each case, the phase of the wave function for each of the 2**p** orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the **phase** of the wave that describes the electron motion, **not** to positive or negative charges.

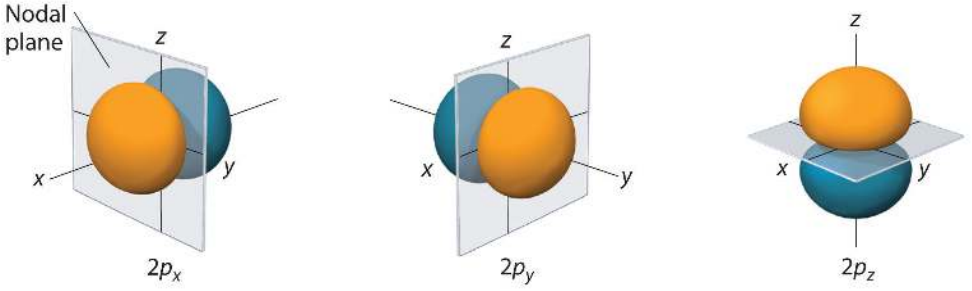


Figure 3.6.4 The Three Equivalent 2**p** Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2\mathbf{p_x}$, $2\mathbf{p_y}$, and $2\mathbf{p_z}$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2**p** orbital. The phase of the wave function is positive (orange) in the region of space where **x**, **y**, or **z** is positive and negative (blue) where **x**, **y**, or **z** is negative. Just as with the **s** orbitals, the size and complexity of the **p** orbitals for any atom increase as the principal quantum number **n** increases. The shapes of the 90% probability surfaces of the 3**p**, 4**p**, and higher-energy **p** orbitals are, however, essentially the same as those shown in Figure 3.6.4.

d Orbitals (l=2)

Subshells with **l** = 2 have five **d** orbitals; the first principal shell to have a **d** subshell corresponds to **n** = 3. The five **d** orbitals have $\mathbf{m_l}$ values of −2, −1, 0, +1, and +2.

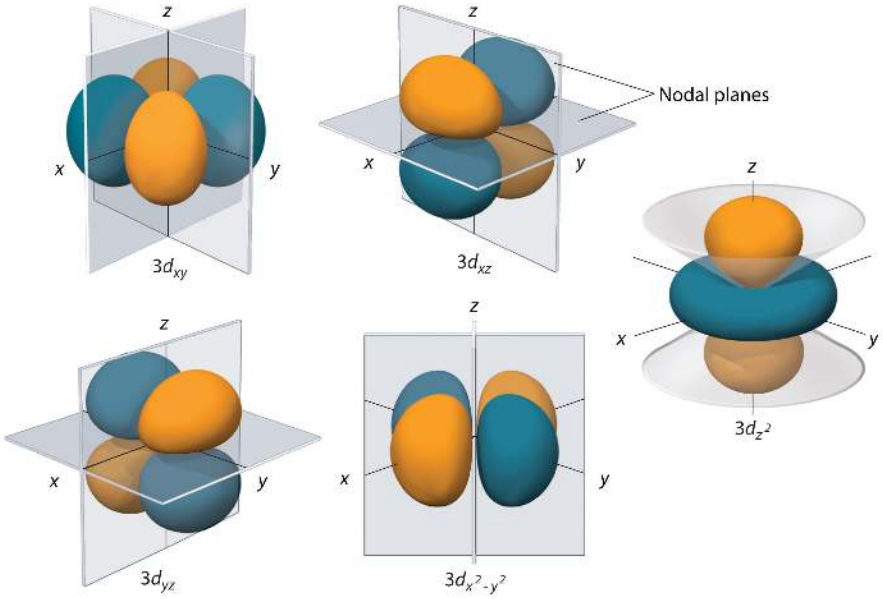


Figure 3.6.5: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The 3 d orbitals can be broken down into 3 d x y, 3 d x z, 3 d y squared, 3 d x squared minus y squared, 3 d z squared.

The hydrogen 3d orbitals, shown in Figure 3.6.5, have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, \)3d_{xz}\), and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 3.6.5, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 3.6.5.

f Orbitals (l=3)

Principal shells with **n** = 4 can have subshells with **l** = 3 and $\mathbf{m_l}$ values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven **f** orbitals. Each **f** orbital has three nodal surfaces, so their shapes are complex. Because **f** orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of **l** are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with **n** ≤ 4 for a hydrogen atom are plotted in Figure 3.6.6; note that the orbital energies depend on **only** the principal quantum number **n**. Consequently, the energies of the 2**s** and 2**p** orbitals of hydrogen are the same; the energies of the 3**s**, 3**p**, and 3**d** orbitals are the same; and so forth. Quantum mechanics predicts that in the hydrogen atom, all orbitals with the same value of **n** (e.g., the three 2**p** orbitals) are **degenerate**, meaning that they have the same energy. The orbital

energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are **4** orbitals with different electron density distributions in the **n** = 2 principal shell (one 2**s** and three 2**p** orbitals), **9** in the **n** = 3 principal shell, and **16** in the **n** = 4 principal shell.The different values of **l** and $\mathbf{m_l}$ for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. Figure 3.6.6 shows that the energy levels become closer and closer together as the value of **n** increases, as expected because of the $1/\mathbf{n}^2$ dependence of orbital energies.

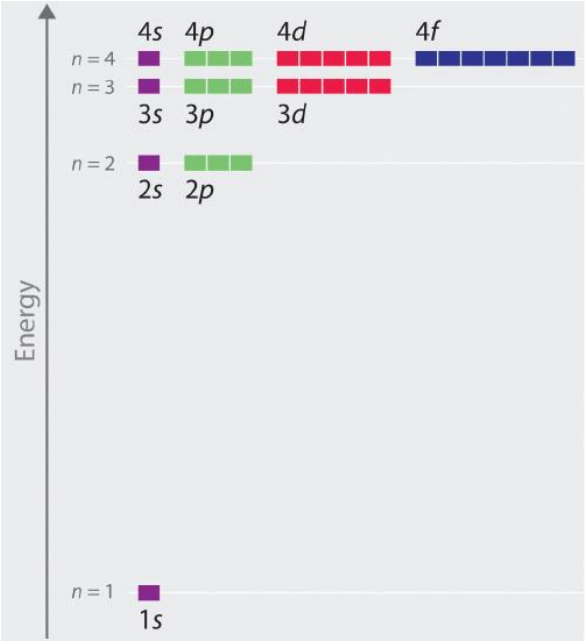


Figure 3.6.6: Orbital Energy Level Diagram for the Hydrogen Atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of **n**.

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation, which can be extended to other single-electron species by incorporating the nuclear charge Z (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2}Rhc \tag{3.6.1}$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Summary

The four chemically important types of atomic orbital correspond to values of $\ell = 0$, 1, 2, and 3. Orbitals with $\ell = 0$ are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $ell = 0$ contain one or more nodes. Orbitals with $\ell = 1$ are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $\ell = 2$ are d orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $\ell = 3$ are f orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2}Rhc$$

In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are degenerate), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

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CHAPTER OVERVIEW

4: Periodic Properties of the Elements

4.1: Aluminum- Low Density Atoms Result in Low Density Metal
4.2: The Periodic Law and The Periodic Table
4.3: Electron Configurations- How Electrons Occupy Orbitals
4.4: Electron Configurations, Valence Electrons, and the Periodic Table
4.5: How Electron Configuration of an Element Relates to this Properties
4.6: Periodic Trends in the Size of Atoms and Effective Nuclear Charge
4.7: Ions- Configurations, Magnetic Properties, Radii, and Ionization Energy
4.8: Electron Affinities and Metallic Character

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4.1: Aluminum- Low Density Atoms Result in Low Density Metal



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4.2: The Periodic Law and 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 4.2.1). 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.

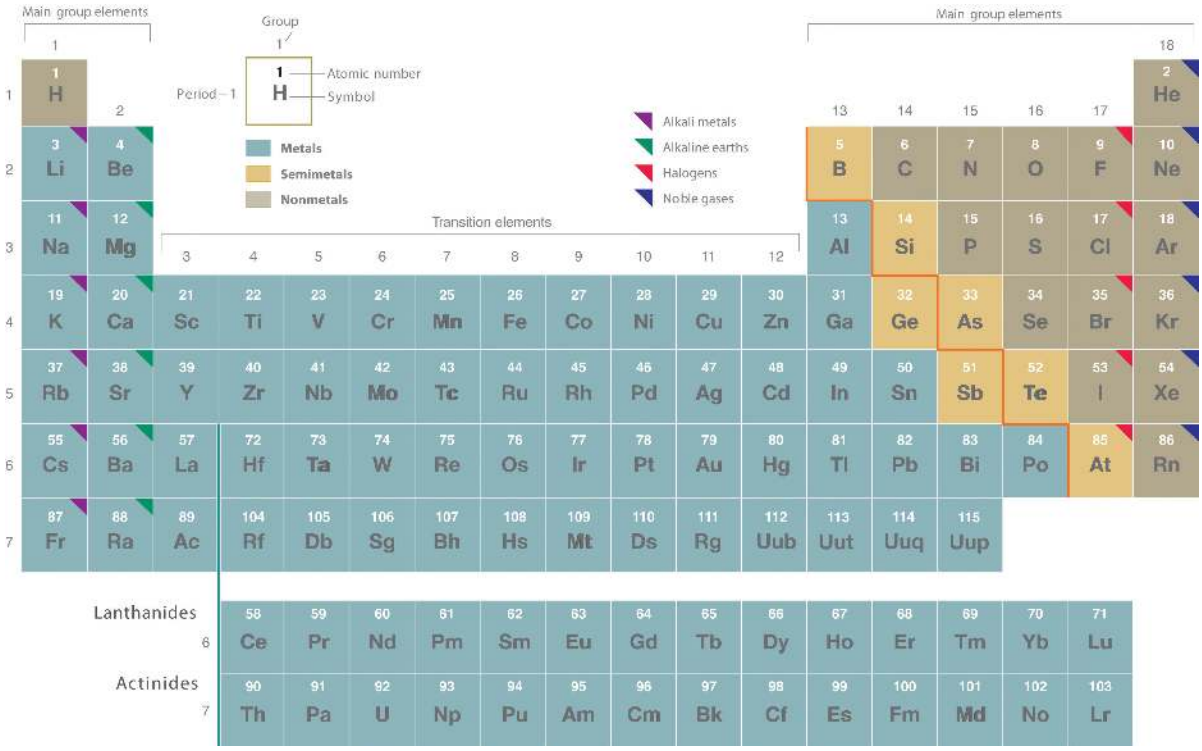


Figure 4.2.1: The Periodic Table Showing the Elements in Order of Increasing Z. The metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals. An interactive Periodic table can be found Periodic Table of the Elements, LibreTexts. (CC-BY-SA-NC 3.0; Anonymous via LibreTexts)

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

Metals, Nonmetals, and Semimetals

The heavy orange zigzag line running diagonally from the upper left to the lower right through groups 13–16 in Figure 4.2.1 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 4.2.1: Classifying Elements

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

Given: element

Asked for: classification

Strategy:

Find selenium in the periodic table shown in Figure 4.2.1 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 4.2.1, 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 4.2.1

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

Answer

metal

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

Group 1: The Alkali Metals

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

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

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

Summary

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

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4.3: Electron Configurations- How Electrons Occupy Orbitals

Learning Objectives

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure 4.3.1 depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

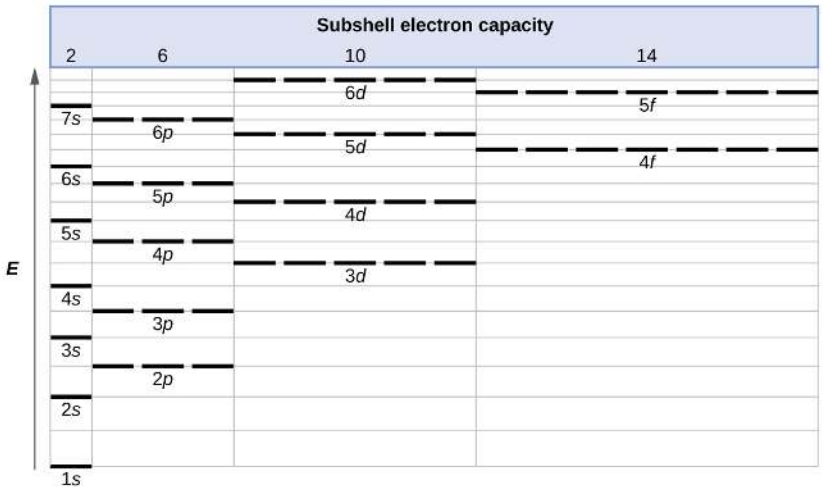


Figure 4.3.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have +*Z* charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 4.3.2):

1. The number of the principal quantum shell, n,
2. The letter that designates the orbital type (the subshell, l), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a p subshell (l = 1) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the d subshell (i.e., l = 2) of the principal shell for which n = 3.

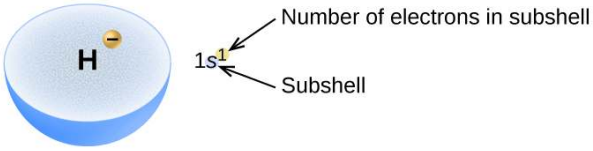


Figure 4.3.2: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 4.3.3), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 4.3.3 illustrates the traditional way to remember the filling order for atomic orbitals.

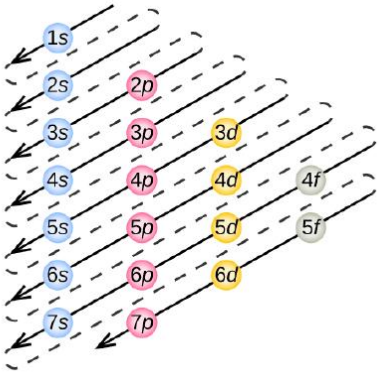


Figure 4.3.3: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

Since the arrangement of the periodic table is based on the electron configurations, Figure 4.3.4 provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing Z order. For example, after filling the 3p block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3d orbitals.

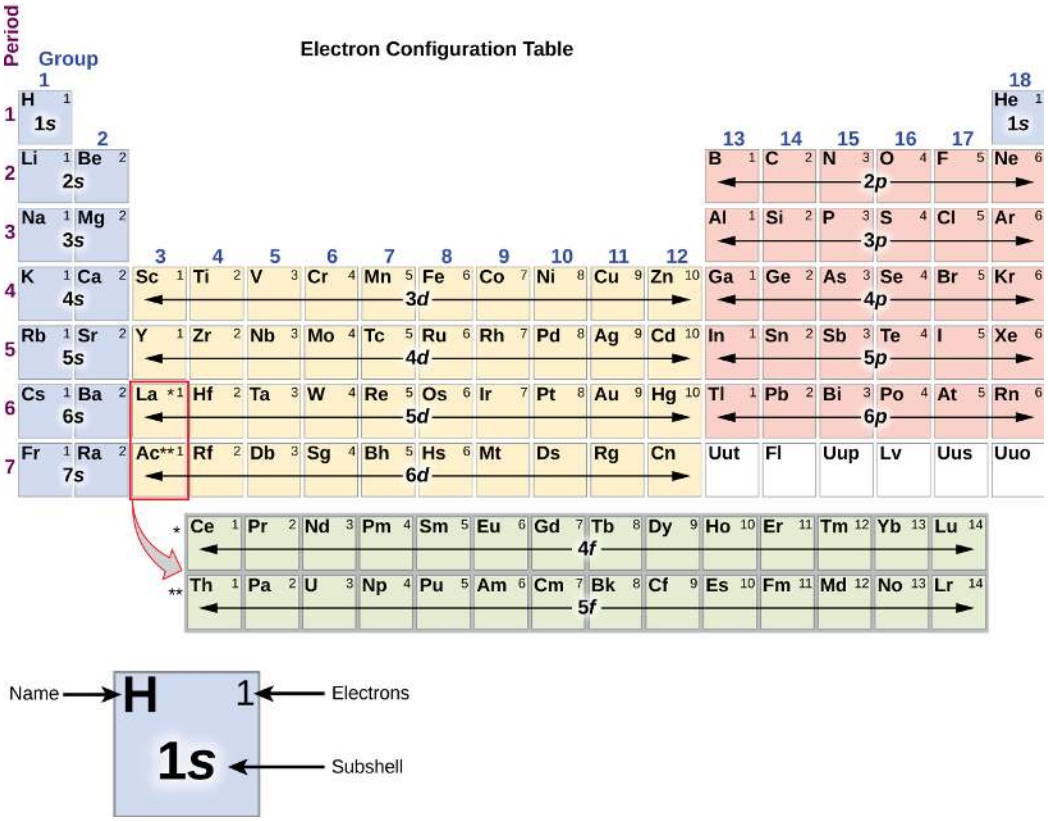
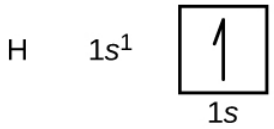
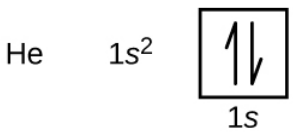


Figure 4.3.4: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure 4.3.3 or 4.3.4, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:



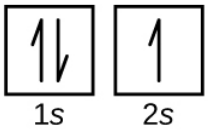
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:



The n = 1 shell is completely filled in a helium atom.

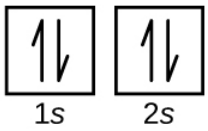
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure 4.3.3 or 4.3.4). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$



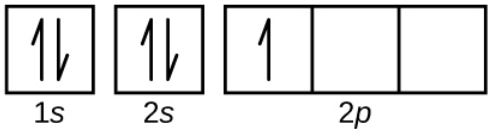
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

Be $1s^2 2s^2$



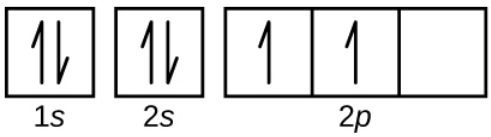
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals ($m_l = -1, 0, +1$) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

B $1s^2 2s^2 2p^1$



Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund's rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical *n*, *l*, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

C $1s^2 2s^2 2p^2$



Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

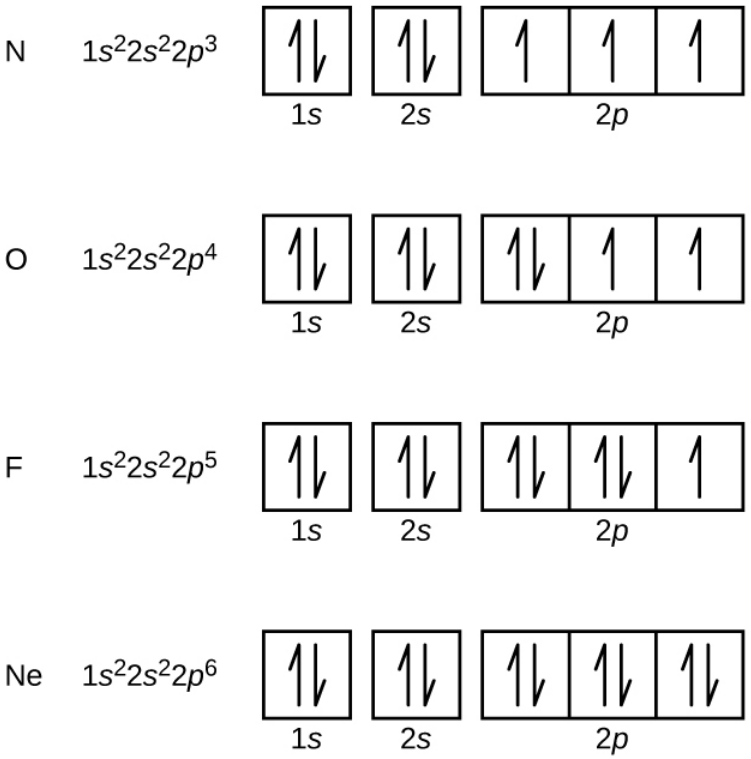


Figure 4.3.5: Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called core electrons (Figure \PageIndex5\PageIndex5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

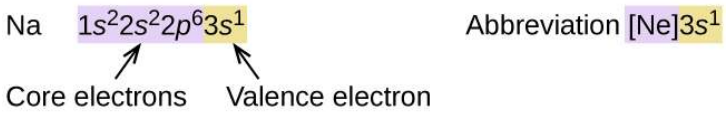


Figure 4.3.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\text{Li} : [\text{He}]\, 2s^1$$
$$\text{Na} : [\text{Ne}]\, 3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^2 3p^1$, is analogous to its family member boron, [He]$2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure 4.3.6 shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

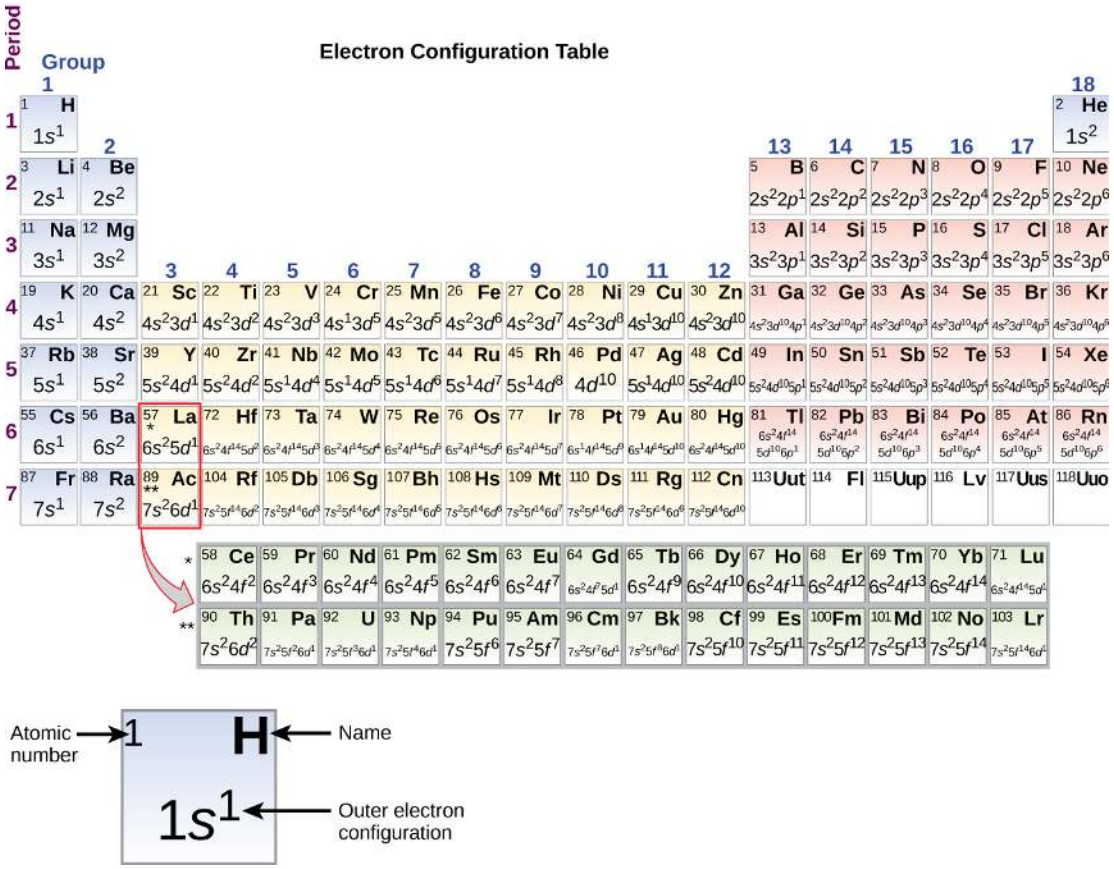


Figure 4.3.6: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure 4.3.3 or 4.3.4). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

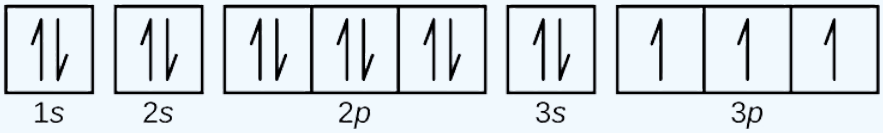
Example 4.3.1: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^2 2s^2 2p^6 3s^2 3p^3$



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 4.3.1

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$

Answer a

Mn

Answer b

Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 4.3.3 or 4.3.4. For instance, the electron configurations of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 4.3.6), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in

an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 4.3.6, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 4.3.6 show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the valence shell, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure 4.3.6. This category includes all the nonmetallic elements, as well as many metals and the intermediate semimetallic elements. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n - 1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 4.3.6) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 4.3.6), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 4.3.6. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the *ns* subshells. There are two inner transition series:
    1. The lanthanide series: lanthanide (La) through lutetium (Lu)
    2. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configurations of Ions

We have seen that ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the $(n - 1)d$ or $(n - 2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

✔ Example 4.3.2: Predicting Electron Configurations of Ions

What is the electron configuration and orbital diagram of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}

e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1 = Na^+$: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.
c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

? Exercise 4.3.2

a. Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$?
b. Which ion with a +3 charge has this configuration?

Answer a

Tc^{2+}

Answer b

Ru^{3+}

Summary

The relative energy of the subshells determine the order in which atomic orbitals are filled (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

Glossary

Aufbau principle
procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

core electron
electron in an atom that occupies the orbitals of the inner shells

electron configuration

electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Hund's rule

every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

orbital diagram

pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

valence electrons

electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom; determine how an element reacts

valence shell

outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest *n* level (*s* and *p* subshells) are in the valence shell, while for transition metals, the highest energy *s* and *d* subshells make up the valence shell and for inner transition elements, the highest *s*, *d*, and *f* subshells are included

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4.4: Electron Configurations, Valence Electrons, and the Periodic Table

Learning Objectives

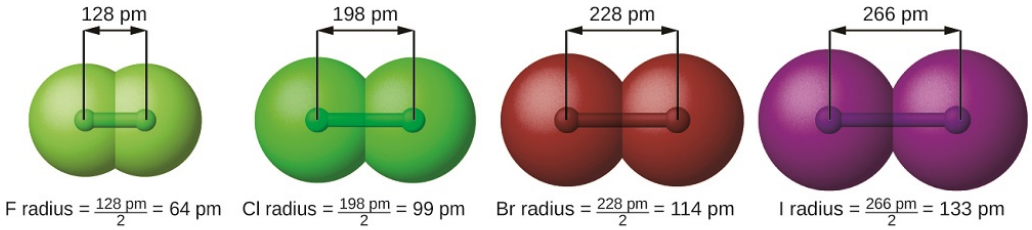
- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of Group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

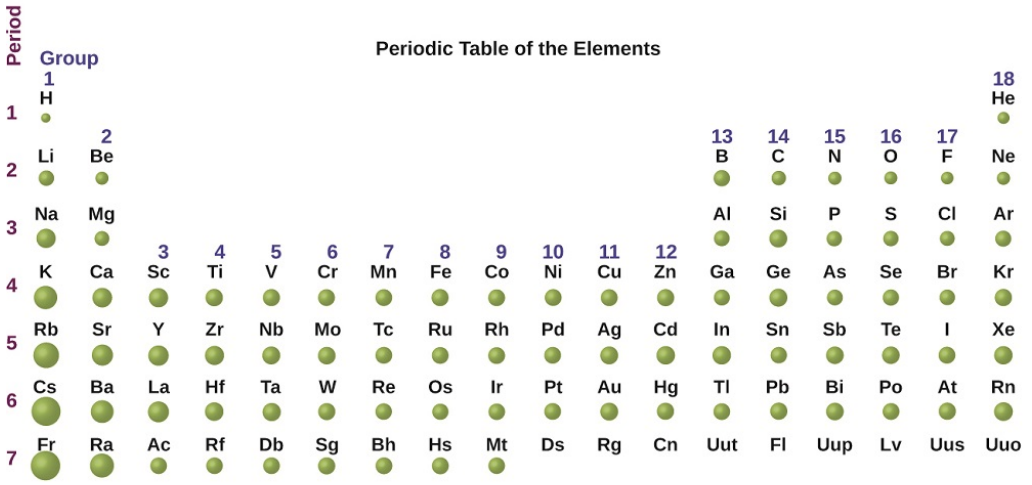
As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 4.4.1), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity).



(a)



(b)

Figure 4.4.1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

This figure has two parts: a and b. In figure a, 4 diatomic molecules are shown to illustrate the method of determining the atomic radius of an atom. The first model, in light green, is used to find the F atom radius. Two spheres are pushed very tightly together. The distance between the centers of the two atoms is indicated above the diagram with a double headed arrow labeled, “128 p m.” The endpoints of this arrow connect to line segments that extend to the atomic radii below. Beneath the molecule is the label, “F radius equals 128 p m divided by 2 equals 64 p m.” The next three models are similarly used to show the atomic radii of additional atoms. The second diatomic molecule is in a darker shade of green. The distance between the radii is 198 p m. Beneath the molecule is the label, “C l radius equals 198 p m divided by 2 equals 99 pm.” The third diatomic molecule is in red. The distance between the radii is 228 p m. Beneath the molecule is the label, “B r radius equals 228 p m divided by 2 equals 114 pm.” The fourth diatomic molecule is in purple. The distance between the radii is 266 p m. Beneath the molecule is the label, “I radius equals 266 p m divided by 2 equals 133 p m.” In figure b, a periodic table layout is used to compare relative sizes of atoms using green spheres. No spheres are provided for the noble or inert gas, group 18 elements. General trends noted are increasing circle size moving from top to bottom in a group, with a general tendency toward increasing atomic radii toward the lower left corner of the periodic table.

We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 4.4.1 and Figure 4.4.1. The trends for the entire periodic table can be seen in Figure 4.4.2.

Table 4.4.1: Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

As shown in Figure 4.4.2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of effective nuclear charge, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - shielding$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

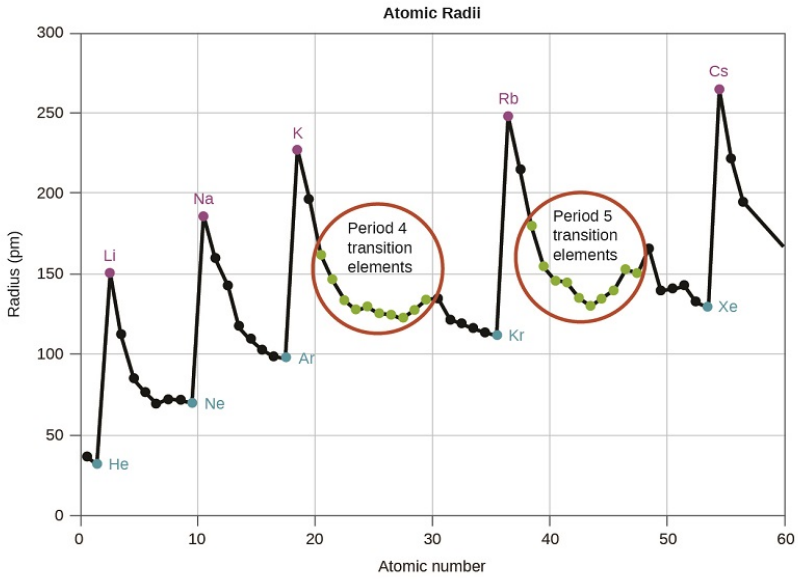


Figure 4.4.2: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

This graph is labeled Atomic Number on the horizontal axis and Radius (p m) on the vertical axis. A black jagged line connects the radii values for elements with atomic numbers 1 through 60 on the graph. Peaks are evident at the locations of the alkali metals: L i, N a, K, R b, and C s. Similarly, minima exist at the locations of noble or inert gases: H e, N e, A r, K r, X e, and R n. The locations of period 4 and period 5 transition elements are provided with green dots.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n - 1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 4.4.1: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

? Exercise 4.4.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 4.4.3). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure 4.4.3: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

The figure includes spheres in green to represent the relative sizes of A l and S atoms. Beneath each of these spheres is a red sphere. The red sphere represents the ionic states of aluminum and sulfur respectively. While radius for the aluminum cation is smaller than aluminum, the sulfur anion has a greater radius than sulfur.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, *n*.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 4.4.3). For example, a sulfur atom ($[Ne]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\mathrm{X}(g) \longrightarrow \mathrm{X}^+(g) + \mathrm{e}^- \quad \mathrm{IE}_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathrm{X}^+(g) \longrightarrow \mathrm{X}^{2+}(g) + \mathrm{e}^- \quad \mathrm{IE}_2$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the

ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

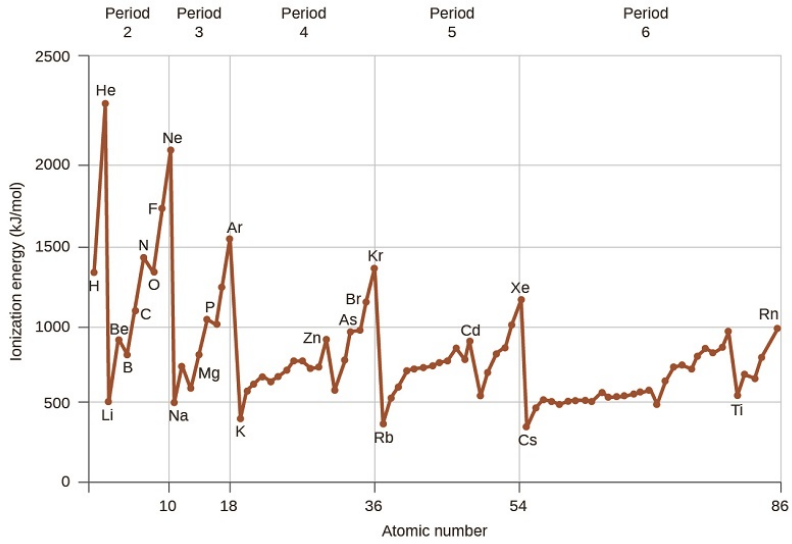


Figure 4.4.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

This figure includes Atomic Number on the horizontal axis and, Ionization Energy (k J divided by mol) on the vertical axis. A red jagged line connects the ionization energies for elements with atomic numbers 1 through 86 on the graph. Peaks are evident at the locations of the noble or inert gases: H e, N e, A r, K r, X e, and R n. Similarly, minima exist at the locations of the alkali metals: L i, N a, K, R b, and C s.

Figure 4.4.4 graphs the relationship between the first ionization energy and the atomic number of several elements. Within a period, the values of first ionization energy for the elements (IE_1) generally increases with increasing Z. Down a group, the IE_1 value generally decreases with increasing Z. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the s electrons are lower in energy than the p electrons. This means that an s electron is harder to remove from an atom than a p electron in the same shell. The electron removed during the ionization of beryllium ($[He]2s^2$) is an s electron, whereas the electron removed during the ionization of boron ($[He]2s^22p^1$) is a p electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

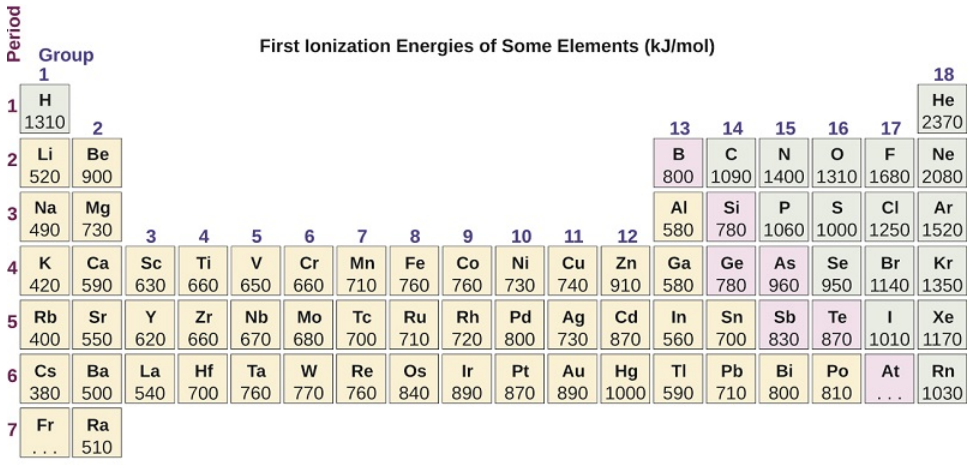
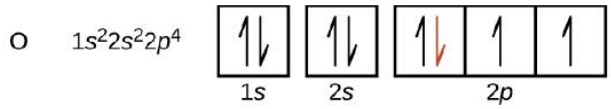


Figure 4.4.5: This version of the periodic table shows the first ionization energy of (IE: $_1$), in kJ/mol, of selected elements.

The trends for first ionization energies across periods and down groups are shown in this version of the periodic table.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 4.4.4.



The electronic configuration for oxygen is 1s superscript 2, 2s superscript, 2p superscript 4. An orbital diagram shows 2 squares each filled with a pair of opposite pointing arrows to represent the 1s ans 2s orbitals. Each of the three connected square which represents the 2p orbitals are filled with one arrow respectively with the addition of 1 red arrow in the first of the three squares.

Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 4.4.2, there is a large increase in the ionization energies (color change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 4.4.2: Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

✔ Example 4.4.2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from

$$Al \quad (Al^{2+} \longrightarrow Al^{3+} + e^-)$$

requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:

$$IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na).$$

? Exercise 4.4.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

Variation in Electron Affinities

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$\mathrm{X}(g) + \mathrm{e}^- \longrightarrow \mathrm{X}^-(g) \quad \mathrm{EA}_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 4.4.6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

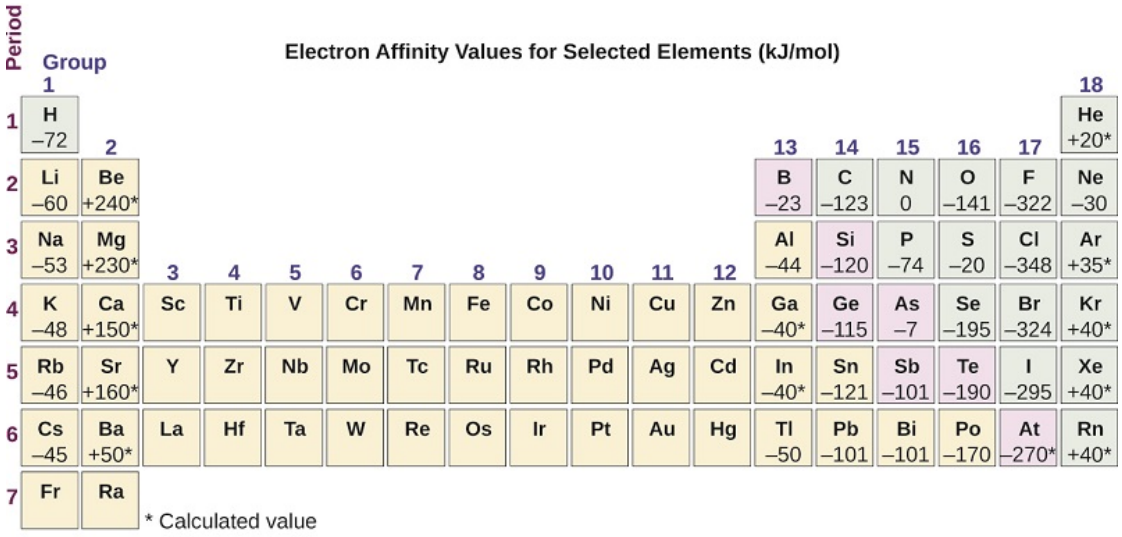


Figure 4.4.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:
The trend for electron affinity values across periods and down groups is shown in this version of the periodic table. Values are not shown for groups 3 to 12 as well as period 7.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the

electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

Glossary

covalent radius
: one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge
: charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity
: energy required to add an electron to a gaseous atom to form an anion

ionization energy
: energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic
: group of ions or atoms that have identical electron configurations

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4.4: Electron Configurations, Valence Electrons, and the Periodic Table is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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4.5: How Electron Configuration of an Element Relates to this Properties



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4.6: Periodic Trends in the Size of Atoms and Effective Nuclear Charge

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes; however, some atoms are larger or smaller than others, and this influences their chemistry. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 4.6.1 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.

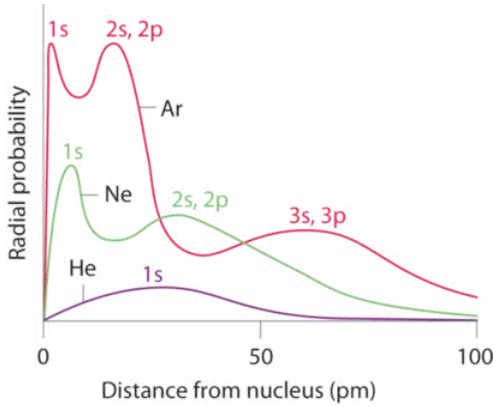


Figure 4.6.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another maximum at ≈35 pm (the $n = 2$ shell). In Ar, the 1*s* electrons have a maximum at ≈2 pm, the 2*s* and 2*p* electrons combine to form a maximum at ≈18 pm, and the 3*s* and 3*p* electrons combine to form a maximum at ≈70 pm.

Figure 4.6.1 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 1*s* 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 4.6.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a **covalent atomic radius** (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure 4.6.2*a*). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1 \text{ Å} = 1 \times 10^{-10} \text{ m} = 100 \text{ pm}$.

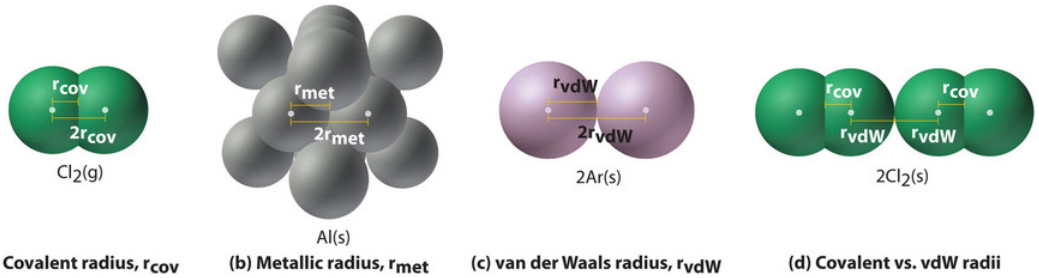


Figure 4.6.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is half the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is half the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds. A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the **metallic atomic radius** (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure 4.6.2*b*). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the **van der Waals atomic radius** (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (Figure 4.6.2*c*). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_2\,(s)$ at low temperatures). These radii are generally not the same (Figure 4.6.2*d*).

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 4.6.3).

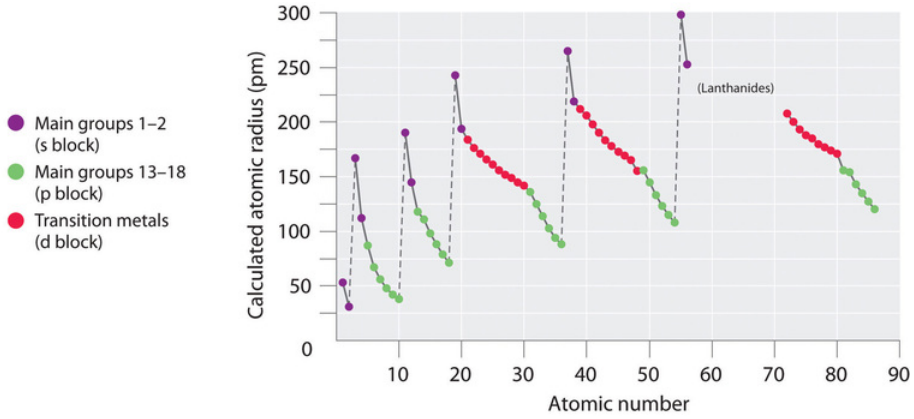


Figure 4.6.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

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 4.6.4).

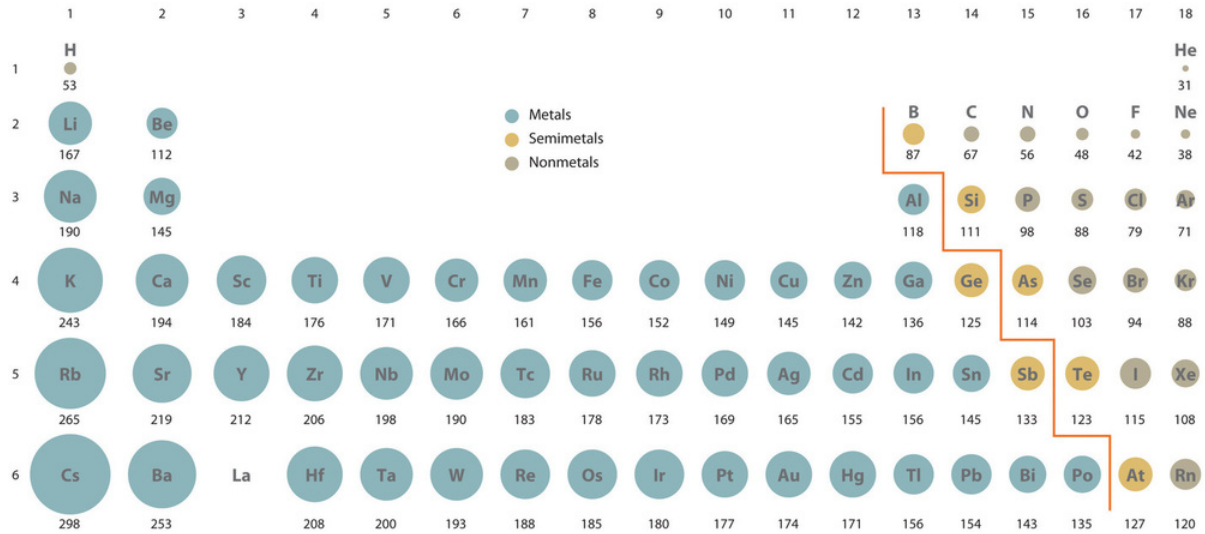


Figure 4.6.4 Calculated Atomic Radii (in Picometers) of the *s*-, *p*-, and *d*-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: Web elements [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties.

Trends in atomic size result from differences in the **effective nuclear charges** (Z_{eff}) experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

> *Atomic radii decrease from left to right across a row and increase from top to bottom down a column.*

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size (Figure 4.6.5).

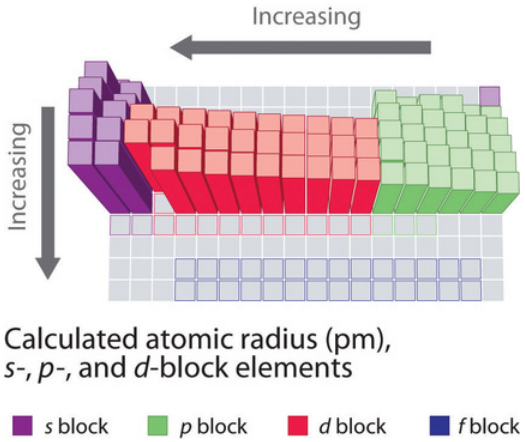


Figure 4.6.5: The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2, the size of the orbitals increases as *n* increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*. However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number *n* increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Not all Electrons shield equally

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example 4.6.1

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.

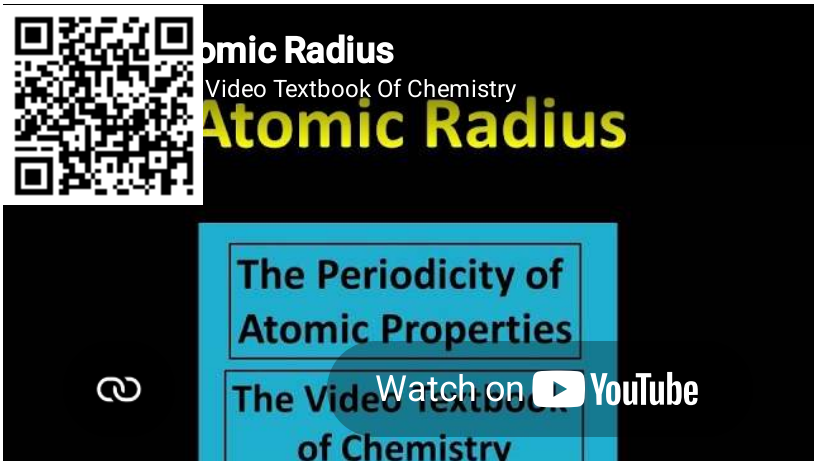
B Combining the two inequalities gives the overall order: C < Si < Al.

? Exercise 4.6.1

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



Atomic Radius: Atomic Radius, YouTube(opens in new window) [youtu.be]

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion). The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

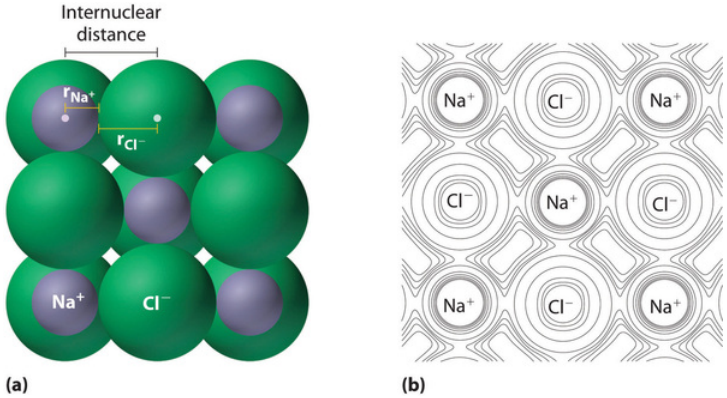


Figure 4.6.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure 4.6.6, the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

A comparison of ionic radii with atomic radii (Figure 4.6.7) shows that *a cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases and the ion shrinks (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases and the ion expands (compare F at 42 pm with F^- at 133 pm).

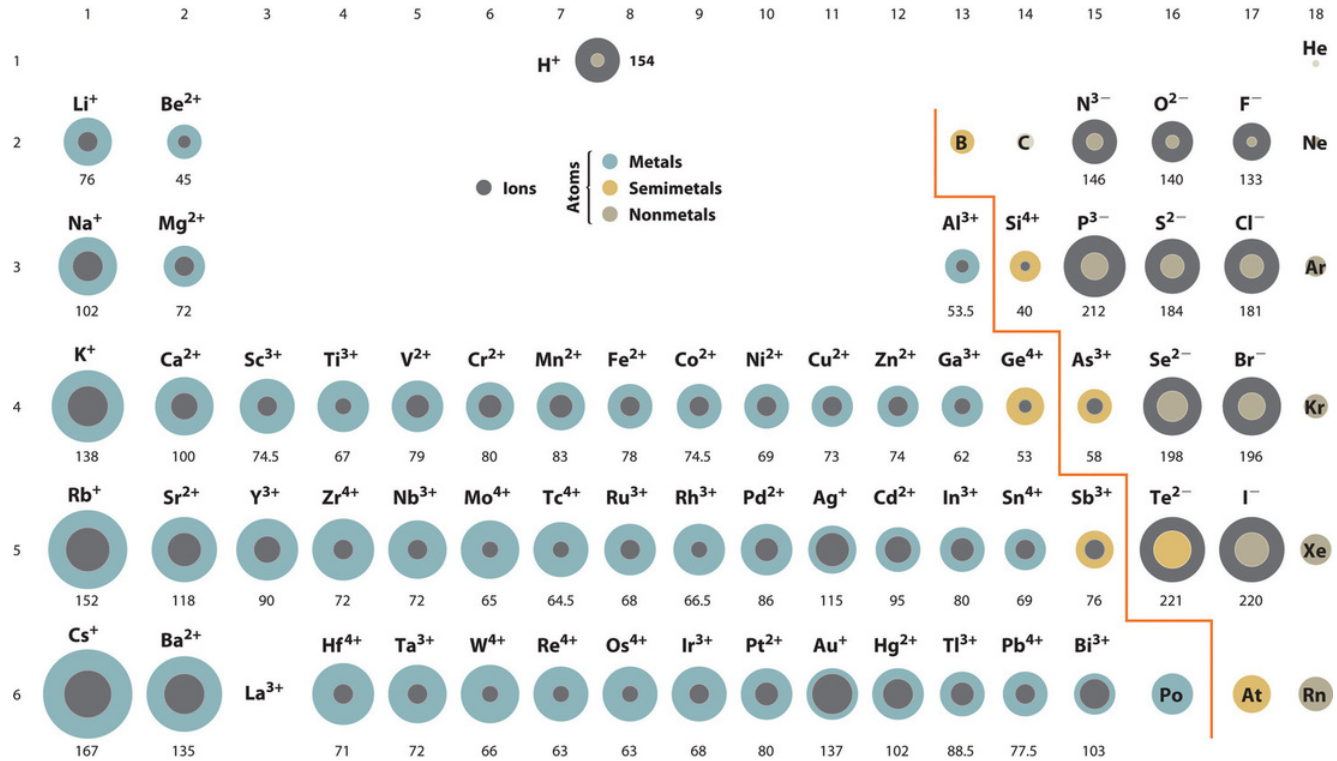


Figure 4.6.7: Ionic Radii (in Picometers) of the Most Common Ionic States of the *s*-, *p*-, and *d*-Block Elements.Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

> *Cations are **always** smaller than the neutral atom and anions are **always** larger.*

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 4.6.1. 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.

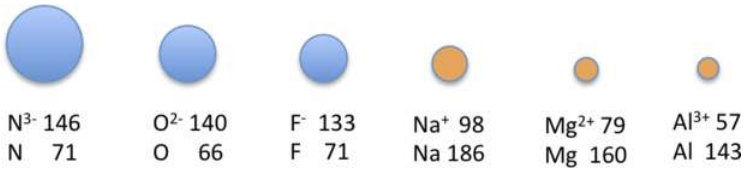
Table 4.6.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	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 4.6.3.



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 4.6.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table 4.6.3: 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 4.6.2

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 4.6.2

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.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Learning Objectives

- To understand the basics of electron shielding and penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at

a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies. These effects are the underlying basis for the periodic trends in elemental properties that we will explore in this chapter.

Electron Shielding and Effective Nuclear Charge

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, many of the other electrons will be *between* that electron and the nucleus (Figure 4.6.1). Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z. This effect is called **electron shielding**.

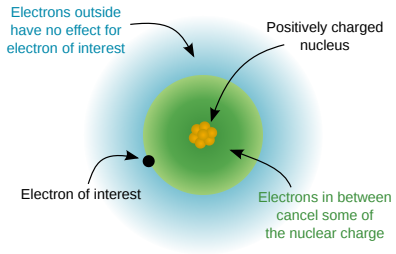


Figure 4.6.1: This image shows how inner electrons can shield outer electrons from the nuclear charge. (CC BY-SA 3.0; NikNaks via Wikipedia).

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z-1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z:

$$1 \leq Z_{eff} \leq Z.$$

Notice that $Z_{eff} = Z$ only for hydrogen (Figure 4.6.2).

Definition: Shielding

Shielding refers to the core electrons repelling the outer electrons, which lowers the effective charge of the nucleus on the outer electrons. Hence, the nucleus has "less grip" on the outer electrons insofar as it is shielded from them.

Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$$Z_{eff} = Z - S \tag{4.6.1}$$

where Z is the atomic number (number of protons in nucleus) and S is the shielding constant and is approximated by number of electrons between the nucleus and the electron in question (*the number of nonvalence electrons*). The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

We can see from Equation 4.6.1 that the effective nuclear charge of an atom increases as the number of protons in an atom increases (Figure 4.6.2). As we will discuss later on in the chapter, this phenomenon can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

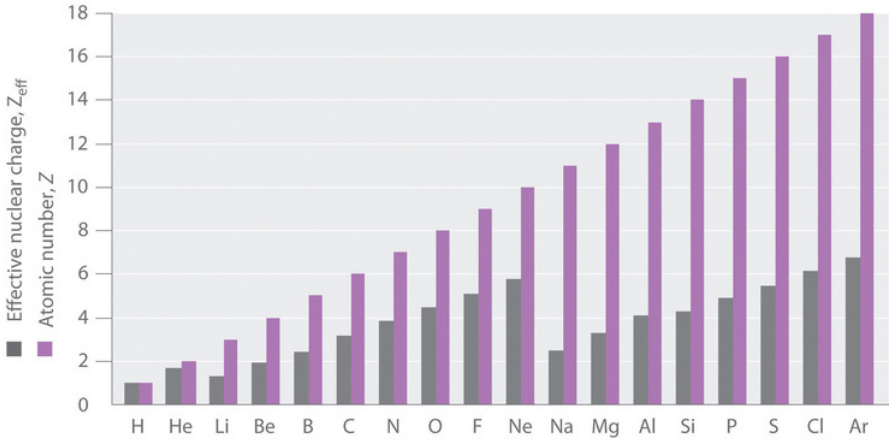


Figure 4.6.2: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the (CC BY-SA-NC 3.0; anonynous)

The shielding constant can be estimated by totaling the screening by **all nonvalence electrons** (n) except the one in question.

$$S = \sum_{i}^{n-1} S_i \tag{4.6.2}$$

where S_i is the shielding of the ith electron.

> *Electrons that are shielded from the full charge of the nucleus experience an effective nuclear charge (Z_{eff}) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ion.*

From Equations 4.6.1 and 4.6.2, Z_{eff} for a specific electron can be estimated is the shielding constants for that electron of all other electrons in species is known. A simple approximation is that all other non-valence electrons shield equally and fully:

$$S_i = 1 \tag{4.6.3}$$

This crude approximation is demonstrated in Example 4.6.1.

Example 4.6.1: Fluorine, Neon, and Sodium

What is the effective attraction Z_{eff} experienced by the valence electrons in the three isoelectronic species: the fluorine anion, the neutral neon atom, and sodium cation?

Solution

Each species has 10 electrons, and the number of nonvalence electrons is 2 (10 total electrons - 8 valence), but the effective nuclear charge varies because each has a different atomic number A. This is an application of Equations 4.6.1 and 4.6.2. We use the simple assumption that all electrons shield equally and fully the valence electrons (Equation 4.6.3).

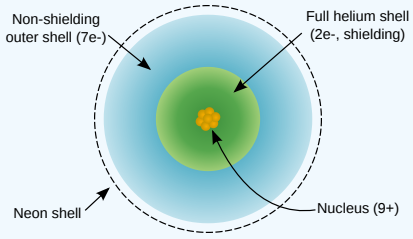


Diagram of a fluorine atom showing the extent of effective nuclear charge. (CC BY-SA 3.0; NikNaks via Wikipedia).

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals.

- $Z_{\text{eff}}(\text{F}^-) = 9 - 2 = 7+$

- $Z_{\text{eff}}(\text{Ne}) = 10 - 2 = 8+$
- $Z_{\text{eff}}(\text{Na}^+) = 11 - 2 = 9+$

So the sodium cation has the greatest effective nuclear charge. This also suggests that Na^+ has the smallest radius of these species and that is correct.

? Exercise 4.6.1: Magnesium Species

What is the effective attraction Z_{eff} experienced by the valence electrons in the magnesium anion, the neutral magnesium atom, and magnesium cation? Use the simple approximation for shielding constants. Compare your result for the magnesium atom to the more accurate value in Figure 4.6.2 and proposed an origin for the difference.

Answer

- $Z_{\text{eff}}(\text{Mg}^-) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}^+) = 12 - 10 = 2+$

Remember that the simple approximations in Equations 4.6.2 and 4.6.3 suggest that valence electrons **do not shield** other valence electrons. Therefore, each of these species has the same number of non-valence electrons and Equation 4.6.1 suggests the effective charge on each valence electron is identical for each of the three species.

This is not correct and a more complex model is needed to predict the experimental observed Z_{eff} value. The ability of valence electrons to shield other valence electrons or in partial amounts (e.g., $S_i \neq 1$) is in violation of Equations 4.6.2 and 4.6.3. That fact that these approximations are poor is suggested by the experimental Z_{eff} value shown in Figure 4.6.2 for Mg of 3.2+. This is appreciably larger than the +2 estimated above, which means these simple approximations overestimate the total shielding constant S. A more sophisticated model is needed.

Electron Penetration

The approximation in Equation 4.6.3 is a good first order description of electron shielding, but the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 4.6.2 for the elements of the first three rows of the periodic table.

Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom (Figure 4.6.3). Electrons in different orbitals have different electron densities around the nucleus. In other words, penetration depends on the shell (n) and subshell (l).

For example, a 1s electron (Figure 4.6.3; purple curve) has greater electron density near the nucleus than a 2p electron (Figure 4.6.3; red curve) and has a greater penetration. This related to the shielding constants since the 1s electrons are closer to the nucleus than a 2p electron, hence the 1s screens a 2p electron almost perfectly ($S = 1$. However, the 2s electron has a lower shielding constant ($S < 1$ because it can penetrate close to the nucleus in the small area of electron density within the first spherical node (Figure 4.6.3; green curve). In this way the 2s electron can "avoid" some of the shielding effect of the inner 1s electron.

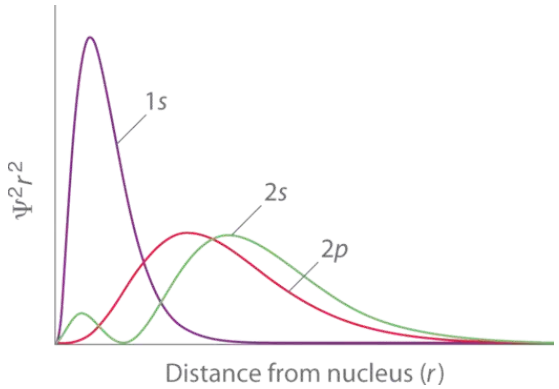


Figure 4.6.3: Orbital Penetration. A comparison of the radial probability distribution of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital. (CC BY-NC-SA 3.0; Anonymous)

For the same shell value (n) the penetrating power of an electron follows this trend in subshells (Figure 4.6.3):

$$s > p > d \approx f. \tag{4.6.4}$$

for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

$$1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f \ \ldots \tag{4.6.5}$$

Definition: Penetration

Penetration describes the proximity of electrons in an orbital to the nucleus. Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity.

Table 4.6.1: Effective Nuclear Charges for Selected Atoms

Atom	Sublevel	Z	Z_{eff}
H	1s	1	1
He	1s	2	1.69
Li	1s, 2s	3	2.69, 1.28
Be	1s, 2s	4	3.68, 1.91
B	1s, 2s, 2p	5	4.68, 2.58, 2.42
F	1s, 2s, 2p	9	8.65, 5.13, 5.10
Na	1s, 2s, 2p, 3s	11	10.63, 6.57, 6.80, 2.51

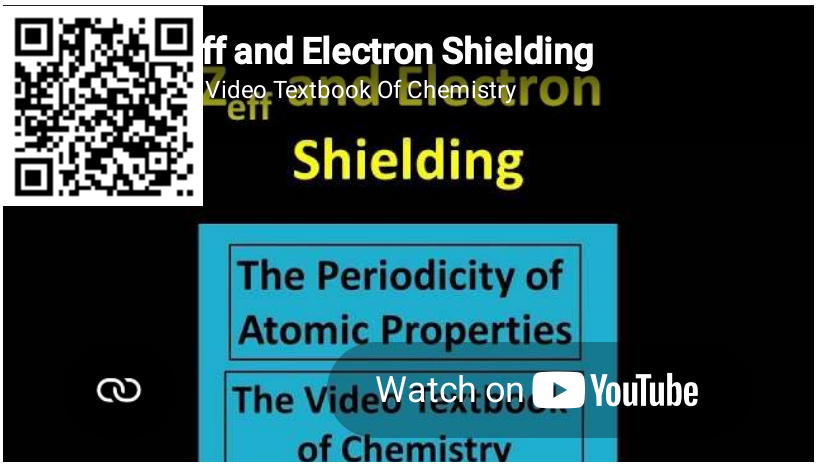
Data from E. Clementi and D. L. Raimondi; The Journal of Chemical Physics 38, 2686 (1963).

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

A Better Estimation of Shielding: Slater Rules

The concepts of electron shielding, orbital penetration and effective nuclear charge were introduced above, but we did so in a qualitative manner (e.g., Equations 4.6.4 and 4.6.5). A more accurate model for estimating electron shielding and corresponding

effective nuclear charge experienced is Slater's Rules. However, the application of these rules is outside the scope of this text.



Zeff and Electron Shielding: Zeff and Electron Shielding(opens in new window) [youtu.be]

Summary

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of *l* and the same value of *n* overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

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4.7: Ions- Configurations, Magnetic Properties, Radii, and Ionization Energy

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. Why is this so? In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad \text{energy required=I} \tag{4.7.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 4.7.1. Larger values of I mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an nth ionization energy (I_n) according to the following reactions:

$$\mathrm{E\,(g)} \rightarrow \mathrm{E^{+}\,(g) + e^{-}} \qquad I_1 = \text{1st ionization energy} \tag{4.7.2}$$

$$\mathrm{E^{+}\,(g)} \rightarrow \mathrm{E^{2+}\,(g) + e^{-}} \qquad I_2 = \text{2nd ionization energy} \tag{4.7.3}$$

$$\mathrm{E^{2+}\,(g)} \rightarrow \mathrm{E^{3+}\,(g) + e^{-}} \qquad I_3 = \text{3rd ionization energy} \tag{4.7.4}$$

Values for the ionization energies of Li and Be listed in Table 4.7.1 show that successive ionization energies for an element increase as they go; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

> *Successive ionization energies for an element **increase**.*

Table 4.7.1: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Reaction	Electronic Transition	I	Reaction	Electronic Transition	I
$\mathrm{Li\,(g) \rightarrow Li^{+}\,(g) + e^{-}}$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2	$\mathrm{Be\,(g) \rightarrow Be^{+}\,(g) + e^{-}}$	$1s^2 2s^2 \rightarrow 1s^2 2s^1$	I_1 = 899.5
$\mathrm{Li^{+}\,(g) \rightarrow Li^{2+}\,(g) + e^{-}}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$\mathrm{Be^{+}\,(g) \rightarrow Be^{2+}\,(g) + e^{-}}$	$1s^2 2s^1 \rightarrow 1s^2$	I_2 = 1757.1
$\mathrm{Li^{2+}\,(g) \rightarrow Li^{3+}\,(g) + e^{-}}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$\mathrm{Be^{2+}\,(g) \rightarrow Be^{3+}\,(g) + e^{-}}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$\mathrm{Be^{3+}\,(g) \rightarrow Be^{4+}\,(g) + e^{-}}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The increase in successive ionization energies, however, is not linear, but increases drastically when removing electrons in lower n orbitals closer to the nucleus. The most important consequence of the values listed in Table 4.7.1 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:

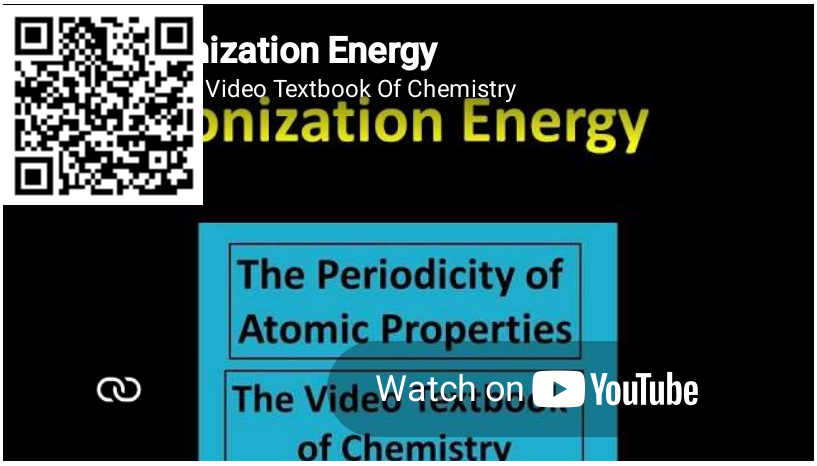
$$Li^+(g) \rightarrow Li^{2+}(g) + e^- \tag{4.7.5}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be:

$$Be^{2+}(g) \rightarrow Be^{3+}(g) + e^- \tag{4.7.6}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 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.*

> *The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.*



Ionization Energy: Ionization Energy, YouTube(opens in new window) [youtu.be] (opens in new window)

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 4.7.2): 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 4.7.2. 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 4.7.2: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	577.4.4	1816.7	2744.8	**11,577.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1907.4.4	2914.1	4963.6	6274.0	**21,267.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,107.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3

*Inner-shell electron

Example 4.7.1: Highest Fourth Ionization Energy

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.

b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^-$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise 4.7.1: 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 4.7.2 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.

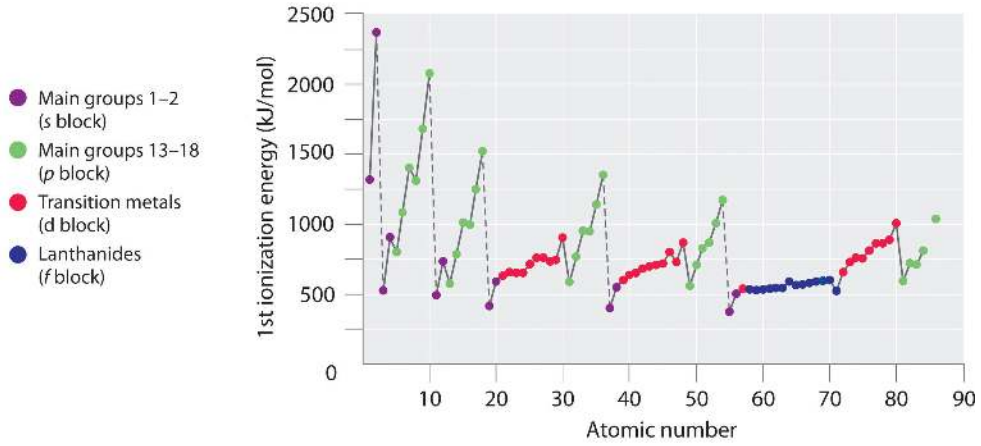


Figure 4.7.1: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

the main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electron configurations of these "exceptions" provide the answer why. The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does and the *p* electron is more easily removed. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

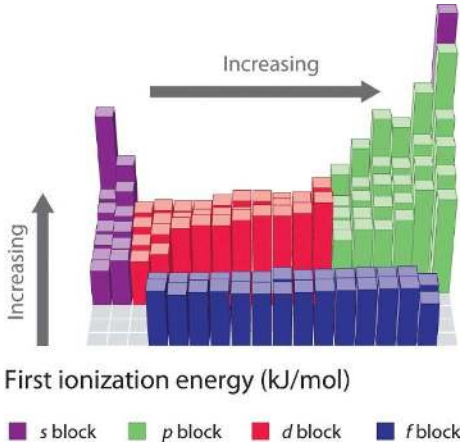


Figure 4.7.2: First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements

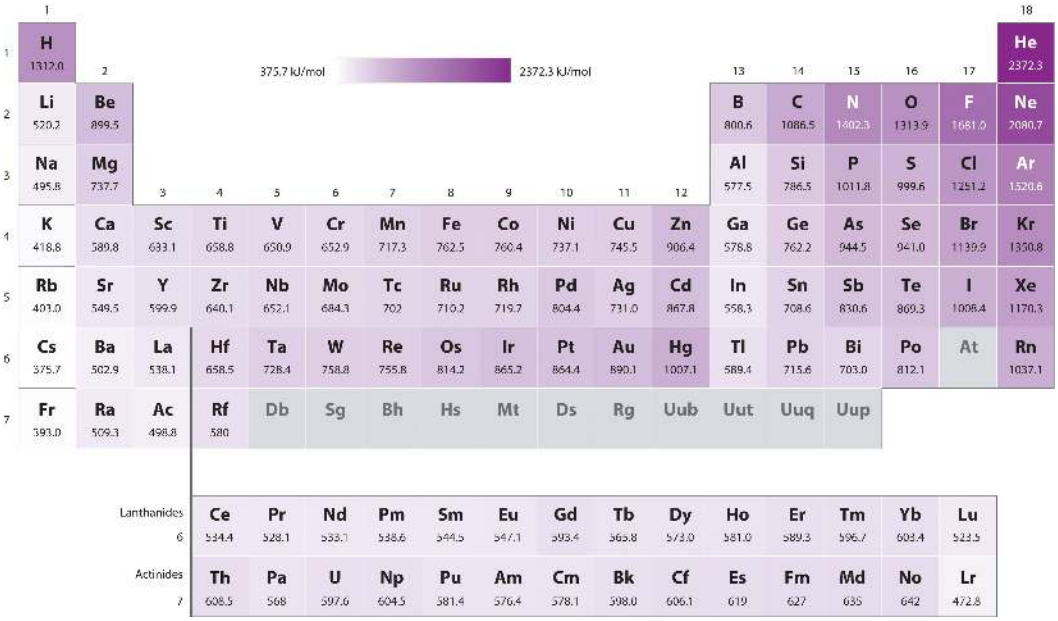
The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. First ionization energy increase from left to right and from bottom to top.

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 4.7.1 and are presented numerically and graphically in Figure 4.7.2. These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the

transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12).

2. First ionization energies generally decrease down a column. Although the principal quantum number n increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius typically corresponds to a lower ionization energy*.
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).



The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

> *Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.*

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: $[Ar]4s^23d^{10}4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the $4p$ subshell, shielding the single $4p$ electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its $[Ar]3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier p-block elements. They are sometimes referred to as *pseudo noble gas configurations*. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the $(n-1)d^{10}$ filled subshell*.

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the s- and p-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the ns electrons before the $(n-1)d$ or $(n-2)f$ electrons, respectively. This means that transition metal cations have $(n-1)d^n$ valence electron configurations, and lanthanide cations have $(n-2)f^n$ valence electron configurations. Because the $(n-1)d$ and $(n-2)f$ shells are closer to the nucleus than the ns shell, the $(n-1)d$ and $(n-2)f$ electrons screen the ns electrons quite effectively, reducing the

effective nuclear charge felt by the *ns* electrons. As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the *ns* electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. In fact, the *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 3*d* orbitals to be slightly lower in energy than the 4*s* orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

✔ Example 4.7.2: 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 4.7.2: 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

Summary

The tendency of an element to lose electrons is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

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4.8: Electron Affinities and Metallic Character

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to add an electron to an atom or ion.
- To recognize the inverse relationship of ionization energies and electron affinities

The electron affinity (EA) of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom or ion:

$$E_{(g)} + e^{-} \rightarrow E^{-}_{(g)} \qquad \text{energy change=}EA \tag{4.8.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released (Figure $4.8.1$).

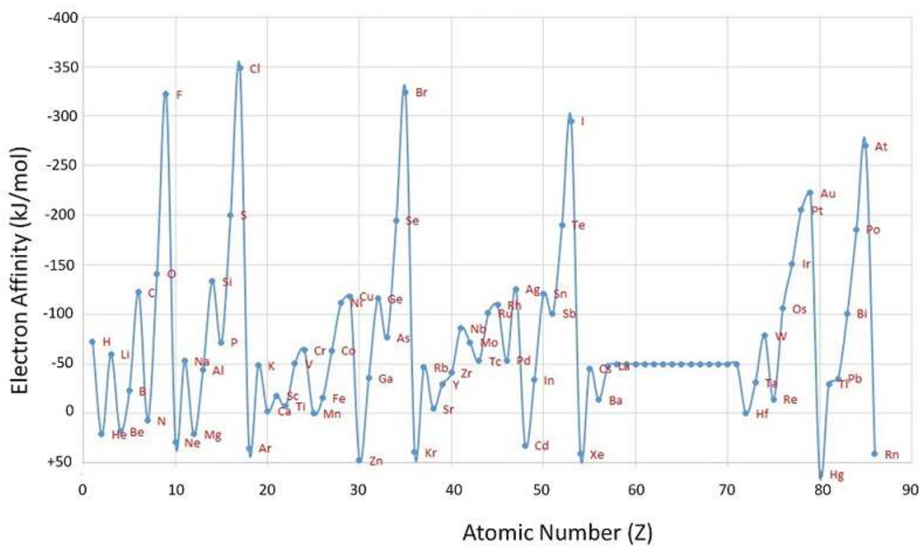


Figure $4.8.1$: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

\[\ce{ Cl(g) + e^- \rightarrow Cl^- (g)} \;\;\;   EA=-346\; kJ/mol \label{7.5.2} \]

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be\,(g) + e^{-} \rightarrow Be^{-}\,(g)} \qquad EA \geq 0 \tag{4.8.2}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$\mathrm{N\,(g) + e^{-} \rightarrow N^{-}\,(g)} \qquad EA \approx 0 \tag{4.8.3}$$

> *Generally, electron affinities become more negative across a row of the periodic table.*

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus.

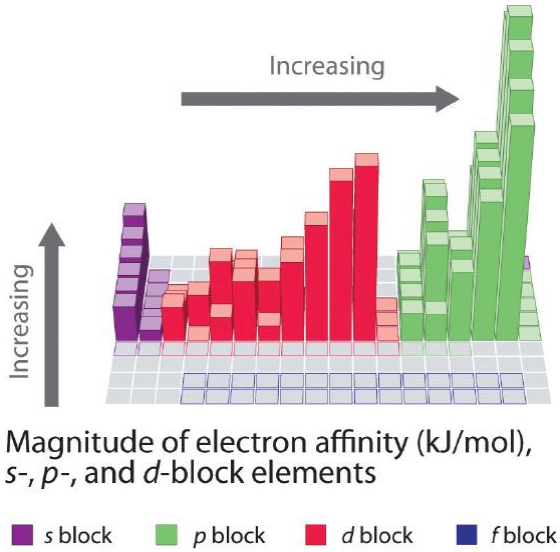


Figure 4.8.2: Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electron affinity increases from left to right and bottom to top.

Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. The energy separation between the filled ns^2 and the empty *np* subshells decreases with increasing *n*, so that formation of an anion from the heavier elements becomes energetically more favorable.

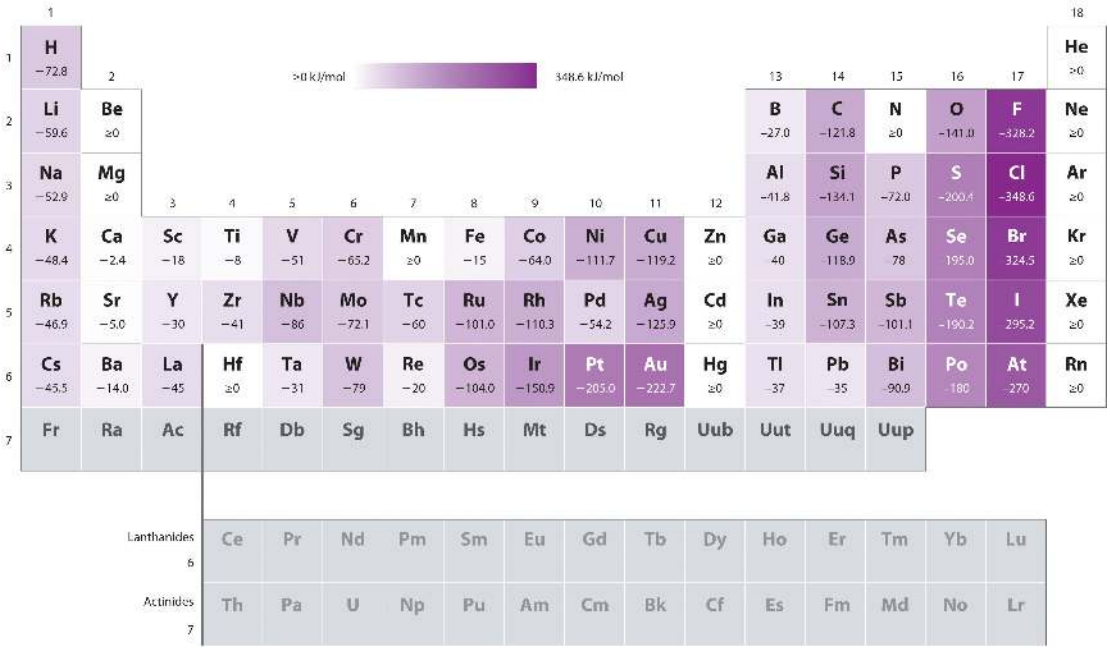


Figure 4.8.3: There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from *Journal of Physical and Chemical Reference Data* 28, no. 6 (1999).

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change}=EA_1 \tag{4.8.4}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change}=EA_2 \tag{4.8.5}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is −141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{4.8.6}$$

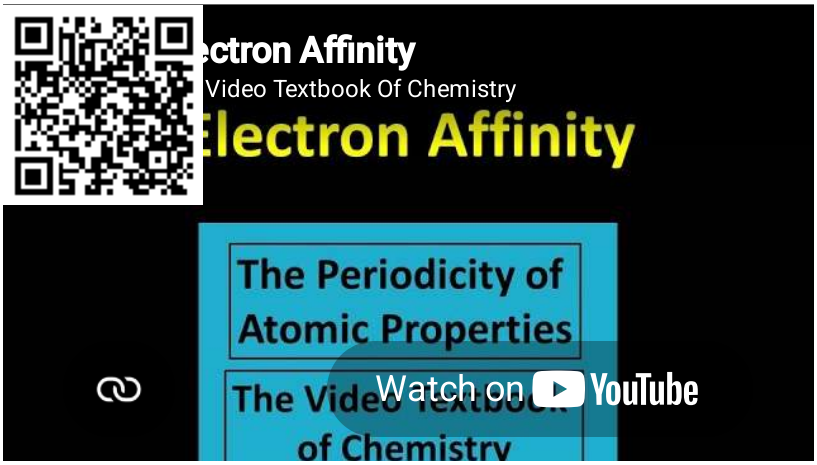
$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{4.8.7}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{4.8.8}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

> *While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.*



Electron Affinity: Electron Affinity, YouTube(opens in new window) [youtu.be] (opens in new window)

If energy is required to form both positively charged cations and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt.*

Example 4.8.1: 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 4.8.1: 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

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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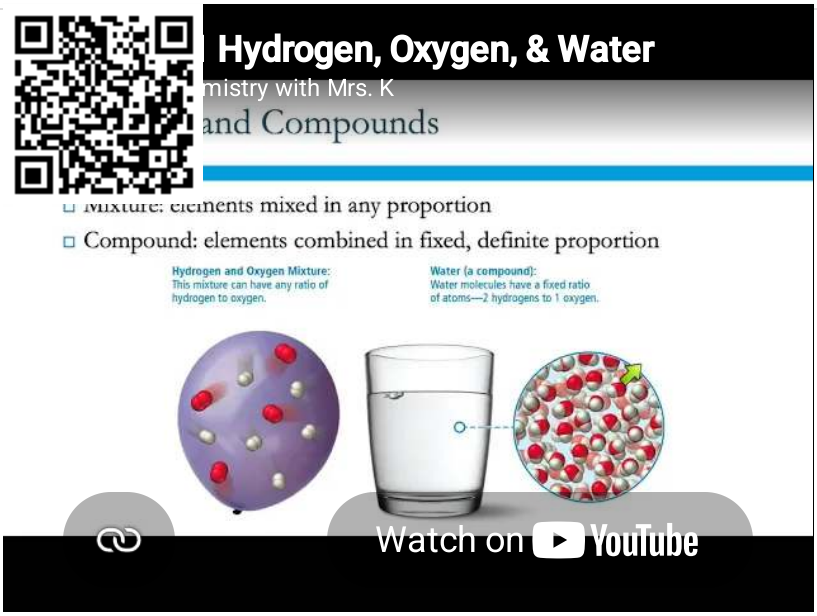
CHAPTER OVERVIEW

5: Molecules and Compounds

5.1: Hydrogen, Oxygen, and Water
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5.1: Hydrogen, Oxygen, and Water



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5.2: Chemical Bonds

Learning Objectives

- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Chemical bonds form when electrons can be simultaneously close to two or more nuclei, but beyond this, there is no simple, easily understood theory that would not only explain why atoms bind together to form molecules, but would also predict the three-dimensional structures of the resulting compounds as well as the energies and other properties of the bonds themselves. Unfortunately, no one theory exists that accomplishes these goals in a satisfactory way for all of the many categories of compounds that are known. Moreover, it seems likely that if such a theory does ever come into being, it will be far from simple.

When we are faced with a scientific problem of this complexity, experience has shown that it is often more useful to concentrate instead on developing **models**. A scientific model is something like a theory in that it should be able to explain observed phenomena and to make useful predictions. But whereas a theory can be discredited by a single contradictory case, a model can be useful even if it does not encompass all instances of the phenomena it attempts to explain. We do not even require that a model be a credible representation of reality; all we ask is that be able to explain the behavior of those cases to which it is applicable in terms that are consistent with the model itself. An example of a model that you may already know about is the kinetic molecular theory of gases. Despite its name, this is really a model (at least at the level that beginning students use it) because it does not even try to explain the observed behavior of real gases. Nevertheless, it serves as a tool for developing our understanding of gases, and as a starting point for more elaborate treatments.Given the extraordinary variety of ways in which atoms combine into aggregates, it should come as no surprise that a number of useful bonding models have been developed. Most of them apply only to certain classes of compounds, or attempt to explain only a restricted range of phenomena. In this section we will provide brief descriptions of some of the bonding models; the more important of these will be treated in much more detail in later parts of this chapter.

Ionic Bonding

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. Ionic bonding is the attraction between positively- and negatively-charged **ions**. These oppositely charged ions attract each other to form ionic networks (or lattices). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

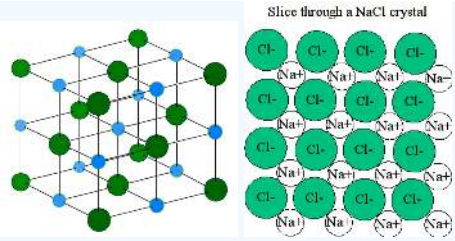
Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

Example 5.2.1: Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

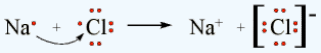
$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)} \tag{5.2.1}$$

These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):



NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattes. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. This can be represented using ***electron-dot symbols*** (here we will consider one chlorine atom, rather than Cl_2):



The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its valence shell:

- Na^+: $2s^2 2p^6$
- Cl^-: $3s^2 3p^6$

Covalent Bonding

Formation of an ionic bond by complete transfer of an electron from one atom to another is possible only for a fairly restricted set of elements. Covalent bonding, in which neither atom loses complete control over its valence electrons, is much more common. In a **covalent bond** the electrons occupy a region of space *between* the two nuclei and are said to be *shared* by them. This model originated with the theory developed by G.N. Lewis in 1916, and it remains the most widely-used model of chemical bonding. The essential element s of this model can best be understood by examining the simplest possible molecule. This is the **hydrogen molecule ion** H_2^+, which consists of two nuclei and one electron. First, however, think what would happen if we tried to make the even simpler molecule H_2^{2+}. Since this would consist only of two protons whose electrostatic charges would repel each other at all distances, it is clear that such a molecule cannot exist; something more than two nuclei are required for bonding to occur.

In the hydrogen molecule ion H_2^+ we have a third particle, an electron. The effect of this electron will depend on its location with respect to the two nuclei. If the electron is in the space between the two nuclei, it will attract both protons toward itself, and thus toward each other. If the total attraction energy exceeds the internuclear repulsion, there will be a net bonding effect and the molecule will be stable. If, on the other hand, the electron is off to one side, it will attract both nuclei, but it will attract the closer one much more strongly, owing to the inverse-square nature of Coulomb's law. As a consequence, the electron will now help the electrostatic repulsion to push the two nuclei apart.

We see, then, that the electron is an essential component of a chemical bond, but that it must be in the right place: between the two nuclei. Coulomb's law can be used to calculate the forces experienced by the two nuclei for various positions of the electron. This allows us to define two regions of space about the nuclei, as shown in the figure. One region, the binding region, depicts locations at which the electron exerts a net binding effect on the new nuclei. Outside of this, in the antibinding region, the electron will actually work against binding.Summary

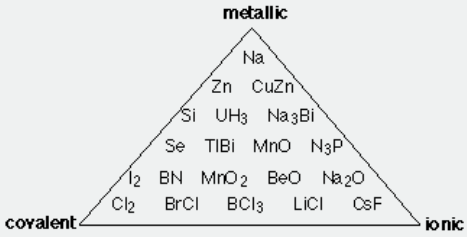
The amount of energy needed to separate a gaseous ion pair is its bond energy. The formation of ionic compounds are usually ***extremely exothermic***. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

Metallic Bonding

Metals have several qualities that are unique, such as the ability to conduct electricity, a low ionization energy, and a low electronegativity (so they will give up electrons easily, i.e., they are cations). **Metallic bonding** is sort of like covalent bonding, because it involves sharing electrons. The simplest model of metallic bonding is the "sea of electrons" model, which imagines that the atoms sit in a sea of valence electrons that are delocalized over all the atoms. Because there are not specific bonds between individual atoms, metals are more flexible. The atoms can move around and the electron sea will keep holding them together. Some metals are very hard and have very high melting points, while others are soft and have low melting points. This depends roughly on the number of valence electrons that form the sea.

A False Dichotomy: The Ionic vs. Colvalent

The covalent-ionic continuum described above is certainly an improvement over the old covalent -*versus* - ionic dichotomy that existed only in the textbook and classroom, but it is still only a one-dimensional view of a multidimensional world, and thus a view that hides more than it reveals. The main thing missing is any allowance for the type of bonding that occurs between more pairs of elements than any other: metallic bonding. Intermetallic compounds are rarely even mentioned in introductory courses, but since most of the elements are metals, there are a lot of them, and many play an important role in metallurgy. In metallic bonding, the valence electrons lose their association with individual atoms; they form what amounts to a mobile "electron fluid" that fills the space between the crystal lattice positions occupied by the atoms, (now essentially positive ions.) The more readily this electron delocalization occurs, the more "metallic" the element.



A triangular diagram whose corners are labeled metallic, covalent, and ionic. The chemical formula of some elements and compounds are listed inside the triangle.

Thus instead of the one-dimension chart shown above, we can construct a triangular diagram whose corners represent the three extremes of "pure" covalent, ionic, and metallic bonding.

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5.4: Ionic Compounds- Formulas and Names

6.9: Binary Ionic Compounds and Their Properties

6.18: Ionic Compounds Containing Polyatomic Ions

Learning Objectives

- Derive names for common types of inorganic compounds using a systematic approach

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are binary compounds, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table 5.4.2.

Table 5.4.1: Names of Some Ionic Compounds

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an *–ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table 5.4.2.

CL, ammonium chloride, C a S O subscript 4 calcium sulfate, and M g subscript 3 (P O subscript 4) subscript 2 magnesium phosphate." data-quail-id="56" data-mt-width="1071">

Table 5.4.2: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Everyday Ionic Compounds

Ionic Compound	Use
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to “iodized” salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
$NaHCO_3$, sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na_2CO_3, sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
$CaCO_3$ calcium carbonate	ingredient in antacids
$Mg(OH)_2$, magnesium hydroxide	ingredient in antacids
$Al(OH)_3$, aluminum hydroxide	ingredient in antacids
NaOH, sodium hydroxide	lye; used as drain cleaner
K_3PO_4, potassium phosphate	food additive (many purposes)
$MgSO_4$, magnesium sulfate	added to purified water
Na_2HPO_4, sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3, sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see [link]), and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 5.4.3.

Table 5.4.3: Names of Some Transition Metal Ionic Compounds

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

a. Fe_2S_3
b. CuSe
c. GaN
d. $CrCl_3$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-}, N^{3-}, Cl^-, and $SO_4{}^{2-}$), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{4+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide
b. copper(II) selenide
c. gallium(III) nitride
d. chromium(III) chloride
e. titanium(III) sulfate

Exercise 5.4.1

Write the formulas of the following ionic compounds:

1. (a) chromium(III) phosphide
2. (b) mercury(II) sulfide
3. (c) manganese(II) phosphate
4. (d) copper(I) oxide
5. (e) chromium(VI) fluoride

Answer

(a) CrP; (b) HgS; (c) $Mn_3(PO_4)_2$; (d) Cu_2O; (e) CrF_6

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion to *–ic*, and adding "acid;" H_2CO_3 is carbonic acid.

Contributors and Attributions

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5.5: Covalent Bonding- Simple Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 5.5.1):

- The electrons in the two atoms repel each other because they have the same charge (
- *The electrons in the two atoms repel each other because they have the same charge (E > 0).*
- *Similarly, the protons in adjacent atoms repel each other (E > 0).*
- *The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa (E < 0). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.*

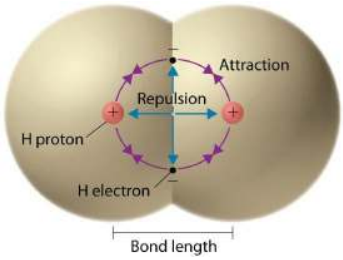


Figure 5.5.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 5.5.2) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures 5.5.1 and 5.5.2, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

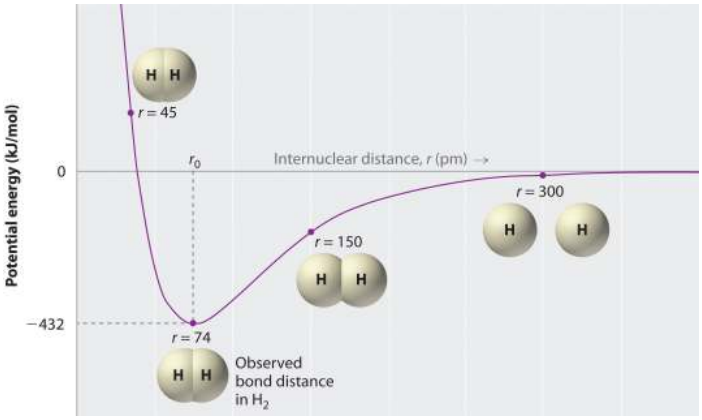


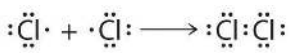
Figure 5.5.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the

internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

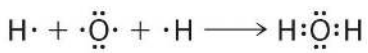
Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.

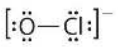
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

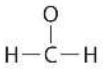
The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



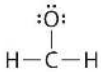
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

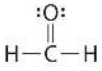
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 5.5.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

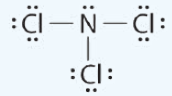
Asked for: Lewis electron structures

Strategy:

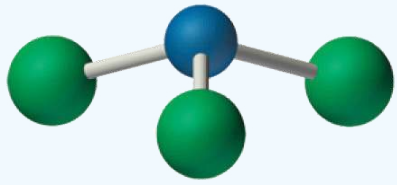
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

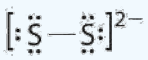


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

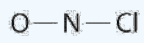


Nitrogen trichloride

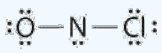
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



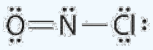
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



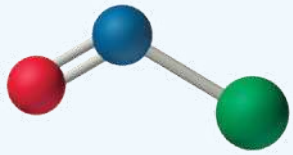
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



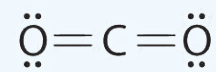
All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



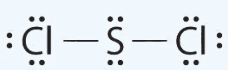
? Exercise 5.5.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

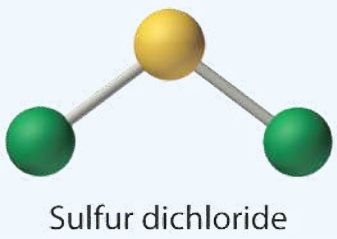
Answer

1. 



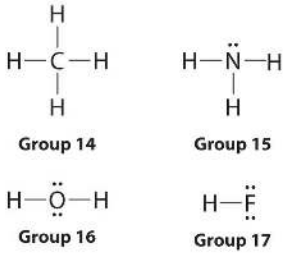
2. 

Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.

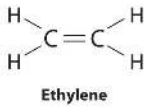


Using Lewis Electron Structures to Explain Stoichiometry

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group 17 (the halogens), this number is one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

> Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 5.5.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

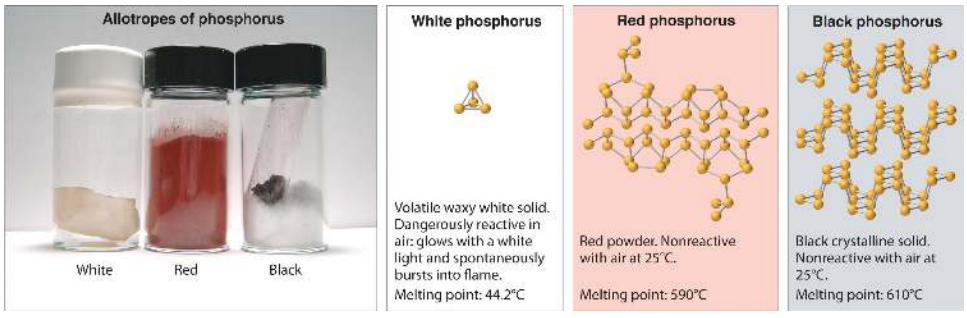


Figure 5.5.3: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure

by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

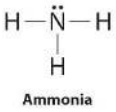
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)} \text{ (atom in Lewis structure)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^-/2)]. Substituting into Equation 5.5.1, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{5.5.1}$$

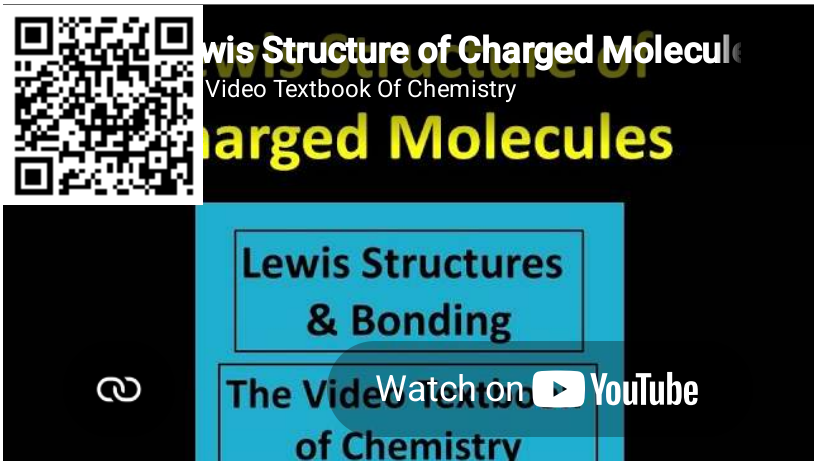
A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 5.5.1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{5.5.2}$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

> An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.



Example 5.5.2: The Ammonium Ion

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

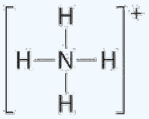
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 5.5.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The central nitrogen is bonded to four hydrogens. The molecule is surrounded by square brackets. Outside the bracket is where the positive charge is placed.

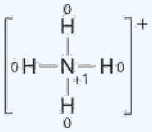
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ???, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus



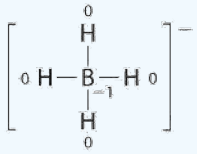
In the Lewis structure, each hydrogen has a zero placed nearby while the nitrogen has a +1 placed nearby.

Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 5.5.2

Write the formal charges on all atoms in BH_4^-.

Answer



Four hydrogens are bonded to a central boron. Each hydrogen has a zero placed nearby while the boron has a -1. The molecule is surrounded by square brackets. Outside of the brackets is a negative charge.

If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

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5.6: The Lewis Model - Representing Valance Electrons with Dots

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.

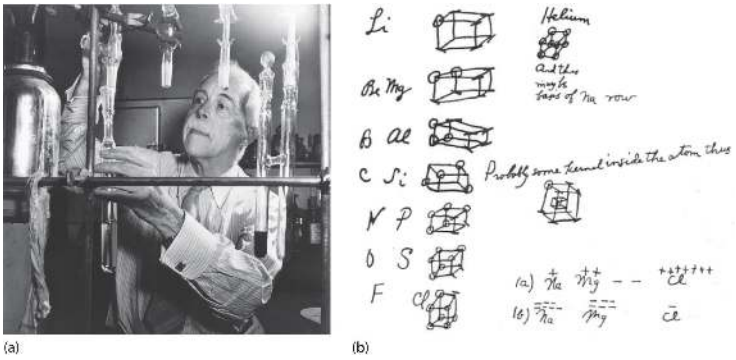


Figure 5.6.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Symbols

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is [Ne]$3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration [He]$2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:

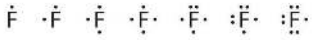


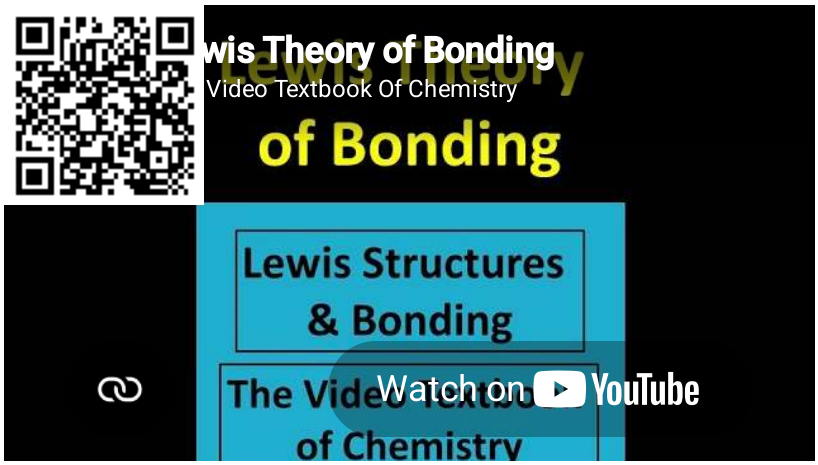
Figure 8.1.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 8.1.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	[He]$2s^1$	Li
Be	[He]$2s^2$	Be
B	[He]$2s^2 2p^1$	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 5.6.2: Lewis Dot Symbols for the Elements in Period 2

L i has one dot on the right, B e has one dot on the left and right, B has one dot on the left, right, and above. C has one dot above, below, on the left and on the right. N has one dot above, below, on the left and two dots on the right. O has two dots on the left and right and one dot above and below. F has two dots above, on the left, on the right and on dot below. N e has two dots above, below, on the right, and on the left.



The Octet Rule

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory. The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability

have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light ;reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the s and p electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Definition: Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., H_2
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., CH_4

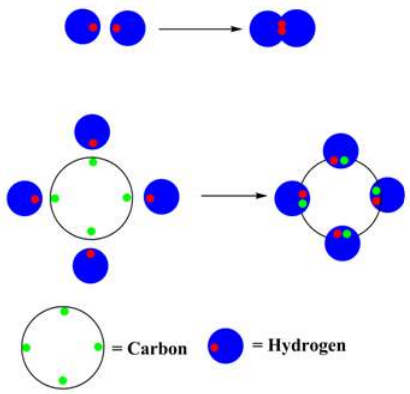


Figure 1: Bonding in H_2 and methane (CH_4)

A hydrogen bonds with each of the four valence electrons of a carbon meaning that four hydrogens can bond with one carbon.

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Example 5.6.1: Salt

The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be

much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

> *Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.*

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.

Summary

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

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5.7: Molecular Compounds- Formulas and Names

Learning Objectives

- Derive names for common types of inorganic compounds using a systematic approach

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table 5.7.3.

Table 5.7.3: Nomenclature Prefixes

Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table 5.7.4.

Table 5.7.4: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride
SO_3	sulfur trioxide		SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide		PF_5	phosphoru

Compound	Name	Compound	Name
			sentafluoride
N_2O_4	dinitrogen tetroxide	P_4O_{10}	tetraphosphorusdecaoxide
N_2O_5	dinitrogen pentoxide	IF_7	iodin

Compound	Name	Compound	Name
			heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

Naming Covalent Compounds

Name the following covalent compounds:

a. SF_6
b. N_2O_3
c. Cl_2O_7
d. P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

a. sulfur hexafluoride
b. dinitrogen trioxide
c. dichlorine heptoxide
d. tetraphosphorus hexoxide

Exercise 5.7.2

Write the formulas for the following compounds:

a. phosphorus pentachloride
b. dinitrogen monoxide
c. iodine heptafluoride
d. carbon tetrachloride

Answer:

(a) PCl_5; (b) N_2O; (c) IF_7; (d) CCl_4

Binary Acids

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

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

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 5.7.5.

Table 5.7.5: Names of Some Simple Acids

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

Oxyacids

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

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

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table 5.7.6. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table 5.7.6: Names of Common Oxyacids

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

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion to *–ic*, and adding "acid;" H_2CO_3 is carbonic acid.

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5.8: Composition of Compounds

Learning Objectives

- To understand the definition and difference between empirical formulas and chemical formulas
- To understand how combustion analysis can be used to identify chemical formulas

Chemical formulas tell you how many atoms of each element are in a compound, and empirical formulas tell you the simplest or most reduced ratio of elements in a compound. If a compound's chemical formula cannot be reduced any more, then the empirical formula is the same as the chemical formula. Combustion analysis can determine the empirical formula of a compound, but cannot determine the chemical formula (other techniques can though). Once known, the chemical formula can be calculated from the empirical formula.

Empirical Formulas

An empirical formula tells us the relative ratios of different atoms in a compound. The ratios hold true on the *molar* level as well. Thus, H_2O is composed of two atoms of hydrogen and 1 atom of oxygen. Likewise, **1.0 mole of H_2O** is composed **of 2.0 moles of hydrogen** and **1.0 mole of oxygen**. We can also work backwards from molar ratios since *if we know the molar amounts of each element in a compound we can determine the empirical formula*.

Example 5.8.1: Mercury Chloride

Mercury forms a compound with chlorine that is 73.9% mercury and 26.1% chlorine by mass. What is the empirical formula?

Solution

Let's say we had a 100 gram sample of this compound. The sample would therefore contain 73.9 grams of mercury and 26.1 grams of chlorine. How many moles of each atom do the individual masses represent?

For Mercury:

$$(73.9\ g) \times \left(\frac{1\ mol}{200.59\ g}\right) = 0.368\ moles$$

For Chlorine:

$$(26.1\ g) \times \left(\frac{1\ mol}{35.45\ g}\right) = 0.736\ mol$$

What is the molar ratio between the two elements?

$$\frac{0.736\ mol\ Cl}{0.368\ mol\ Hg} = 2.0$$

Thus, we have twice as many moles (i.e. atoms) of Cl as Hg. The empirical formula would thus be (remember to list cation first, anion last):

$$HgCl_2$$

Chemical Formula from Empirical Formula

The chemical formula for a compound obtained by composition analysis is always the empirical formula. We can obtain the chemical formula from the empirical formula if we know the molecular weight of the compound. The chemical formula will always be some *integer multiple* of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula). The general flow for this approach is shown in Figure 5.8.1 and demonstrated in Example 5.8.2.

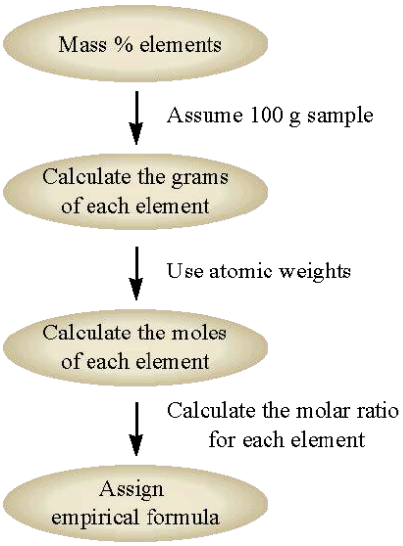


Figure 5.8.1: The general flow chart for solving empirical formulas from known mass percentages.

Flowchart. From mass % elements, calculate the grams of each element. Then, use atomic weights to calculate the moles of each element. Then, assign empirical formula by calculating the molar ratio for each element.

Example 5.8.2: Ascorbic Acid

Vitamin C (ascorbic acid) contains 40.92 % C, 4.58 % H, and 54.50 % O, by mass. The experimentally determined molecular mass is 176 amu. What is the empirical and chemical formula for ascorbic acid?

Solution

Consider an arbitrary amount of 100 grams of ascorbic acid, so we would have:

- 40.92 grams C
- 4.58 grams H
- 54.50 grams O

This would give us how many moles of each element?

- Carbon

$$(40.92\ \cancel{g\,C}) \times \left(\frac{1\ mol\ C}{12.011\ \cancel{g\,C}}\right) = 3.407\ mol\ C$$

- Hydrogen

$$(4.58\ \cancel{g\,H}) \times \left(\frac{1\ mol\ H}{1.008\ \cancel{g\,H}}\right) = 4.544\ mol\ H$$

- Oxygen

$$(54.50\ \cancel{g\,O}) \times \left(\frac{1\ mol\ O}{15.999\ \cancel{g\,O}}\right) = 3.406\ mol\ O$$

Determine the simplest whole number ratio by dividing by the smallest molar amount (3.406 moles in this case - see oxygen):

- Carbon

$$C = \frac{3.407\ mol}{3.406\ mol} \approx 1.0$$

- Hydrogen

$$C = \frac{4.544\ mol}{3.406\ mol} = 1.333$$

- Oxygen

$$C = \frac{3.406\ mol}{3.406\ mol} = 1.0$$

The relative molar amounts of carbon and oxygen appear to be equal, but the relative molar amount of hydrogen is higher. Since we cannot have "fractional" atoms in a compound, we need to normalize the relative amount of hydrogen to be equal to an integer. 1.333 would appear to be 1 and 1/3, so if we multiply the relative amounts of each atom by '3', we should be able to get integer values for each atom.

C = (1.0)*3 = 3

H = (1.333)*3 = 4

O = (1.0)*3 = 3

or

$$C_3H_4O_3$$

This is our ***empirical formula*** for ascorbic acid.

What about the chemical formula? We are told that the experimentally determined molecular mass is **176 *amu***. What is the molecular mass of our empirical formula?

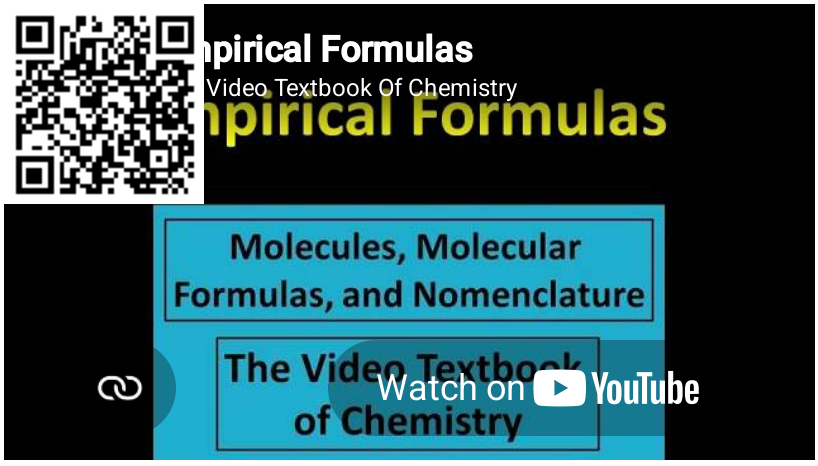
(3*12.011) + (4*1.008) + (3*15.999) = 88.062 *amu*

The molecular mass from our empirical formula is significantly lower than the experimentally determined value. What is the ratio between the two values?

(176 *amu*/88.062 *amu*) = 2.0

Thus, it would appear that our empirical formula is essentially one half the mass of the actual molecular mass. If we multiplied our empirical formula by '2', then the molecular mass would be correct. Thus, the actual chemical formula is:

2* $C_3H_4O_3$ = **$C_6H_8O_6$**



Empirical Formulas: Empirical Formulas, YouTube(opens in new window) [youtu.be]

Combustion Analysis

When a compound containing carbon and hydrogen is subject to combustion with oxygen in a special combustion apparatus all the carbon is converted to CO_2 and the hydrogen to H_2O (Figure 5.8.2). The amount of carbon produced can be determined by measuring the amount of CO_2 produced. This is trapped by the sodium hydroxide, and thus we can monitor the mass of CO_2

produced by determining the increase in mass of the CO_2 trap. Likewise, we can determine the amount of H produced by the amount of H_2O trapped by the magnesium perchlorate.

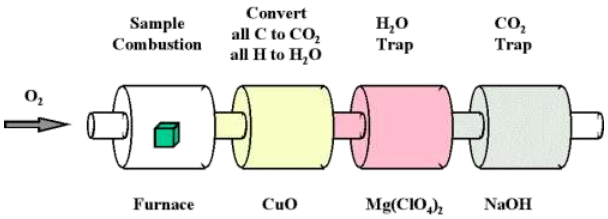


Figure 5.8.2: Combustion analysis apparatus

Diagram of a combustion chamber. O 2 enters the furnace and combusts the sample. All carbon is converted to C O 2 and all hydrogen is converted to H 2 O in the presence of C u O in the next chamber. The next chamber is an H 2 O trap with M g (C l O 4) 2 inside. The next chamber is a C O 2 trap with N a O H inside.

One of the most common ways to determine the elemental composition of an unknown hydrocarbon is an analytical procedure called combustion analysis. A small, carefully weighed sample of an unknown compound that may contain carbon, hydrogen, nitrogen, and/or sulfur is burned in an oxygen atmosphere,Other elements, such as metals, can be determined by other methods. and the quantities of the resulting gaseous products (CO_2, H_2O, N_2, and SO_2, respectively) are determined by one of several possible methods. One procedure used in combustion analysis is outlined schematically in Figure 5.8.3 and a typical combustion analysis is illustrated in Examples 5.8.3 and 5.8.4.

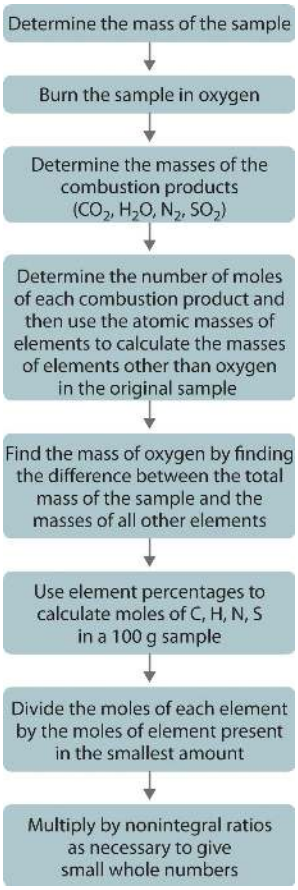


Figure 5.8.3: Steps for Obtaining an Empirical Formula from Combustion Analysis. (CC BY-NC-SA; anonymous)

Example 5.8.3: Combustion of Isopropyl Alcohol

What is the empirical formulate for isopropyl alcohol (which contains only C, H and O) if the combustion of a 0.255 grams isopropyl alcohol sample produces 0.561 grams of CO_2 and 0.306 grams of H_2O?

Solution

From this information quantitate the amount of C and H in the sample.

$$(0.561\ \cancel{g\ CO_2}) \left(\frac{1\ mol\ CO_2}{44.0\ \cancel{g\ CO_2}} \right) = 0.0128\ mol\ CO_2$$

Since one mole of CO_2 is made up of one mole of C and two moles of O, if we have 0.0128 moles of CO_2 in our sample, then we know we have 0.0128 moles of C in the sample. How many grams of C is this?

$$(0.0128\ \cancel{mol\ C}) \left(\frac{12.011\ g\ C}{1\ \cancel{mol\ C}} \right) = 0.154\ g\ C$$

How about the hydrogen?

$$(0.306\ \cancel{g\ H_2O}) \left(\frac{1\ mol\ H_2O}{18.0\ \cancel{g\ H_2O}} \right) = 0.017\ mol\ H_2O$$

Since one mole of H_2O is made up of one mole of oxygen and ***two*** moles of hydrogen, if we have 0.017 moles of H_2O, then we have 2*(0.017) = 0.034 moles of hydrogen. Since hydrogen is about 1 gram/mole, we must have **0.034 grams of hydrogen** in our original sample.

When we add our carbon and hydrogen together we get:

0.154 grams (C) + 0.034 grams (H) = **0.188 grams**

But we know we combusted *0.255 grams* of isopropyl alcohol. The 'missing' mass must be from the oxygen atoms in the isopropyl alcohol:

0.255 grams - 0.188 grams = 0.067 grams oxygen

This much oxygen is how many moles?

$$(0.067\ \cancel{g\ O}) \left(\frac{1\ mol\ O}{15.994\ \cancel{g\ O}} \right) = 0.0042\ mol\ O$$

Overall therefore, we have:

- 0.0128 moles Carbon
- 0.0340 moles Hydrogen
- 0.0042 moles Oxygen

Divide by the smallest molar amount to normalize:

- C = 3.05 atoms
- H = 8.1 atoms
- O = 1 atom

Within experimental error, the most likely empirical formula for propanol would be C_3H_8O

Example 5.8.4: Combustion of Naphalene

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of CO_2 and 11.30 mg of H_2O. Determine the empirical formula of naphthalene.

Given: mass of sample and mass of combustion products

Asked for: empirical formula

Strategy:

A. Use the masses and molar masses of the combustion products, CO_2 and H_2O, to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.
B. Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

Solution:

A Upon combustion, 1 mol of CO_2 is produced for each mole of carbon atoms in the original sample. Similarly, 1 mol of H_2O is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original sample can be calculated from these ratios, the masses of CO_2 and H_2O, and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

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

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

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

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

B To obtain the relative numbers of atoms of both elements present, we need to calculate the number of moles of each and divide by the number of moles of the element present in the smallest amount:

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

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

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

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

Thus naphthalene contains a 1.25:1 ratio of moles of carbon to moles of hydrogen: $C_{1.25}H_{1.0}$. Because the ratios of the elements in the empirical formula must be expressed as small whole numbers, multiply both subscripts by 4, which gives C_5H_4 as the empirical formula of naphthalene. In fact, the chemical formula of naphthalene is $C_{10}H_8$, which is consistent with our results.

? Exercise 5.8.4

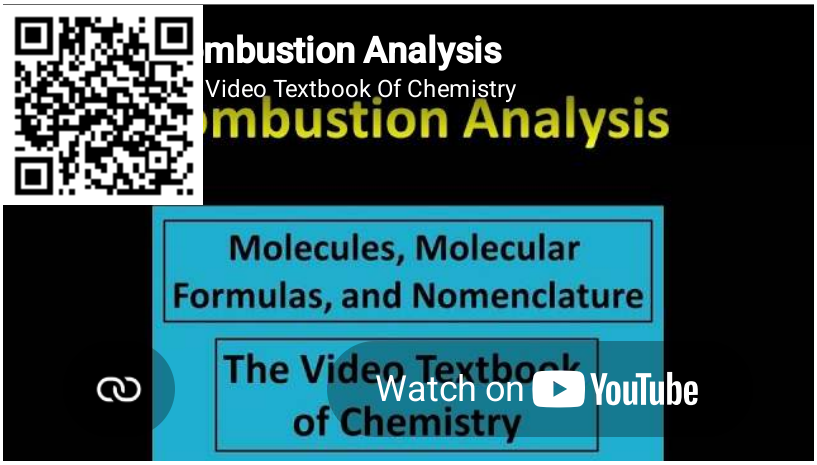
a. Xylene, an organic compound that is a major component of many gasoline blends, contains carbon and hydrogen only. Complete combustion of a 17.12 mg sample of xylene in oxygen yielded 56.77 mg of CO_2 and 14.53 mg of H_2O. Determine the empirical formula of xylene.
b. The empirical formula of benzene is CH (its chemical formula is C_6H_6). If 10.00 mg of benzene is subjected to combustion analysis, what mass of CO_2 and H_2O will be produced?

Answer a

The empirical formula is C_4H_5. (The chemical formula of xylene is actually C_8H_{10}.)

Answer b

33.81 mg of CO_2; 6.92 mg of H_2O



Combustion Analysis: Combustion Analysis, YouTube(opens in new window) [youtu.be]

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5.9: Determining a Chemical Formula from Experimental Data

In the previous section, we discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, we were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

Molecular formulas are derived by comparing the compound's molecular or molar mass to its empirical formula mass. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molecular (or molar) mass of the substance, we can divide this by the empirical formula mass in order to identify the number of empirical formula units per molecule, which we designate as *n*:

$$\frac{\text{molecular or molar mass}\left(\text{amu or }\frac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or }\frac{\text{g}}{\text{mol}}\right)} = n\ \text{formula units/molecule} \tag{5.9.1}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by *n*, as shown by the generic empirical formula A_xB_y:

Double subscripts: use braces to clarify

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180\ \text{amu/molecule}}{30\ \frac{\text{amu}}{\text{formula unit}}} = 6\ \text{formula units/molecule} \tag{5.9.2}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(CH_2O)_6 = C_6H_{12}O_6 \tag{5.9.3}$$

Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, we are merely considering one mole of empirical formula units and molecules, as opposed to single units and molecules.

Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02 \text{ g C}) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 6.163 \text{ mol C} \tag{5.9.4}$$

$$(8.710 \text{ g H}) \left(\frac{1 \text{ mol H}}{1.01 \text{ g H}} \right) = 8.624 \text{ mol H} \tag{5.9.5}$$

$$(17.27 \text{ g N}) \left(\frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 1.233 \text{ mol N} \tag{5.9.6}$$

Next, we calculate the molar ratios of these elements.

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

We calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57 \text{ g nicotine}}{0.2500 \text{ mol nicotine}} = \frac{162.3 \text{ g}}{\text{mol}}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3 \text{ g/mol}}{81.13 \dfrac{\text{g}}{\text{formula unit}}} = 2 \text{ formula units/molecule}$$

Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_6 = C_{10}H_{14}N_2$$

Exercise 5.9.5

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

Answer

$C_8H_{10}N_4O_2$

Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

Combustion Analysis

When a compound containing carbon and hydrogen is subject to combustion with oxygen in a special combustion apparatus all the carbon is converted to CO_2 and the hydrogen to H_2O (Figure 5.9.2). The amount of carbon produced can be determined by measuring the amount of CO_2 produced. This is trapped by the sodium hydroxide, and thus we can monitor the mass of CO_2 produced by determining the increase in mass of the CO_2 trap. Likewise, we can determine the amount of H produced by the amount of H_2O trapped by the magnesium perchlorate.

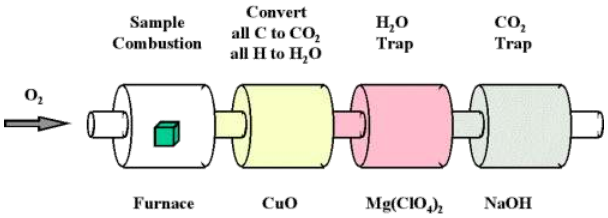


Figure 5.9.2***:*** *Combustion analysis apparatus*

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 5.9.3 and a typical combustion analysis is illustrated in Examples 5.9.3 and 5.9.4.

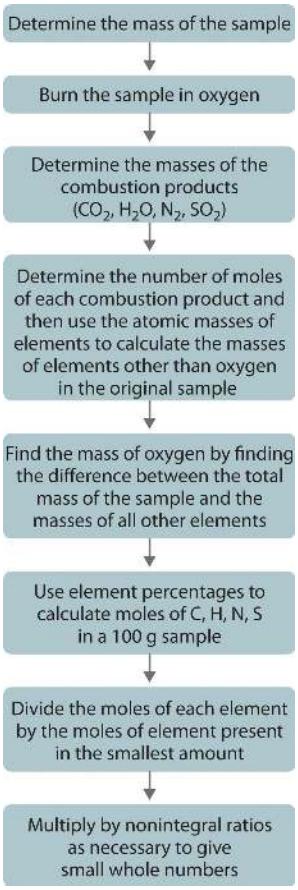


Figure 5.9.3: Steps for Obtaining an Empirical Formula from Combustion Analysis

Example 5.9.3: Combustion of Isopropyl Alcohol

What is the empirical formulate for isopropyl alcohol (which contains only C, H and O) if the combustion of a 0.255 grams isopropyl alcohol sample produces 0.561 grams of CO_2 and 0.306 grams of H_2O?

Solution

From this information quantitate the amount of C and H in the sample.

$$(0.561\ \cancel{g\ CO_2}) \left(\frac{1\ mol\ CO_2}{44.0\ \cancel{g\ CO_2}} \right) = 0.0128\ mol\ CO_2 \tag{5.9.7}$$

Since one mole of CO_2 is made up of one mole of C and two moles of O, if we have 0.0128 moles of CO_2 in our sample, then we know we have 0.0128 moles of C in the sample. How many grams of C is this?

$$(0.0128 \ \cancel{mol\ C}) \left(\frac{12.011\ g\ C}{1\ \cancel{mol\ C}} \right) = 0.154\ g\ C \tag{5.9.8}$$

How about the hydrogen?

$$(0.306 \ \cancel{g\ H_2O}) \left(\frac{1\ mol\ H_2O}{18.0\ \cancel{g\ H_2O}} \right) = 0.017\ mol\ H_2O \tag{5.9.9}$$

Since one mole of H_2O is made up of one mole of oxygen and ***two*** moles of hydrogen, if we have 0.017 moles of H_2O, then we have 2*(0.017) = 0.034 moles of hydrogen. Since hydrogen is about 1 gram/mole, we must have **0.034 grams of hydrogen** in our original sample.

When we add our carbon and hydrogen together we get:

0.154 grams (C) + 0.034 grams (H) = **0.188 grams**

But we know we combusted *0.255 grams* of isopropyl alcohol. The 'missing' mass must be from the oxygen atoms in the isopropyl alcohol:

0.255 grams - 0.188 grams = 0.067 grams oxygen

This much oxygen is how many moles?

$$(0.067 \ \cancel{g\ O}) \left(\frac{1\ mol\ O}{15.994\ \cancel{g\ O}} \right) = 0.0042\ mol\ O \tag{5.9.10}$$

Overall therefore, we have:

- 0.0128 moles Carbon
- 0.0340 moles Hydrogen
- 0.0042 moles Oxygen

Divide by the smallest molar amount to normalize:

- C = 3.05 atoms
- H = 8.1 atoms
- O = 1 atom

Within experimental error, the most likely empirical formula for propanol would be C_3H_8O

Example 5.9.4: Combustion of Naphalene

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of CO_2 and 11.30 mg of H_2O. Determine the empirical formula of naphthalene.

Given: mass of sample and mass of combustion products

Asked for: empirical formula

Strategy:

A. Use the masses and molar masses of the combustion products, CO_2 and H_2O, to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.
B. Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

Solution:

A Upon combustion, 1 mol of CO**2** is produced for each mole of carbon atoms in the original sample. Similarly, 1 mol of H_2O is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original

sample can be calculated from these ratios, the masses of CO_2 and H_2O, and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

$$\underset{mass\,of\,C}{} = 69.00\,mg\,CO_2 \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,CO_2}{44.010\,g\,CO_2} \times \frac{1\,molC}{1\,mol\,CO_2} \times \frac{12.011\,g}{1\,mol\,C} \tag{5.9.11}$$

$$= 1.883 \times 10^{-2}\,g\,C \tag{5.9.12}$$

$$\underset{mass\,of\,H}{} = 11.30\,mg\,H_2O \times \frac{1\,g}{1000\,mg} \times \frac{1\,mol\,H_2O}{18.015\,g\,H_2O} \times \frac{2\,molH}{1\,mol\,H_2O} \times \frac{1.0079\,g}{1\,mol\,H} \tag{5.9.13}$$

$$= 1.264 \times 10^{-3}\,g\,H \tag{5.9.14}$$

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:

$$moles\,C = 1.883 \times 10^{-2}\,g\,C \times \frac{1\,mol\,C}{12.011\,g\,C} = 1.568 \times 10^{-3}\,molC \tag{5.9.15}$$

$$moles\,H = 1.264 \times 10^{-3}\,g\,H \times \frac{1\,mol\,H}{1.0079\,g\,H} = 1.254 \times 10^{-3}\,molH \tag{5.9.16}$$

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

$$H: \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \quad C: \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250 \tag{5.9.17}$$

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 5.9.4

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}.)

Answer b

33.81 mg of CO_2; 6.92 mg of H_2O

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

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5.10: Formula Mass and the Mole Concept for Compounds



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5.11: Organic Compounds

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Organic substances have been used throughout this text to illustrate the differences between ionic and covalent bonding and to demonstrate the intimate connection between the structures of compounds and their chemical reactivity. You learned, for example, that even though NaOH and alcohols (ROH) both have OH in their formula, NaOH is an ionic compound that dissociates completely in water to produce a basic solution containing Na^+ and OH^- ions, whereas alcohols are covalent compounds that do not dissociate in water and instead form neutral aqueous solutions. You also learned that an amine (RNH_2), with its lone pairs of electrons, is a base, whereas a carboxylic acid (RCO_2H), with its dissociable proton, is an acid.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{5.11.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and **inorganic chemistry** is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 5.11.1.

Table 5.11.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
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 5.11.1 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 5.11.1.

Key Takeaway

- Organic chemistry is the study of carbon compounds, nearly all of which also contain hydrogen atoms.

Hydrocarbons

Learning Objectives

- Identify alkanes, alkenes, alkynes, and aromatic compounds.
- List some properties of hydrocarbons.

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called **hydrocarbons**. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons.

Aliphatic hydrocarbons are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are hydrocarbons that contain at least one C–C double bond, and **Alkynes** are hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called *cycloalkanes* (or *cycloalkenes* or *cycloalkynes*).

Aromatic hydrocarbons have a special six-carbon ring called a *benzene* ring. Electrons in the benzene ring have special energetic properties that give benzene physical and chemical properties that are markedly different from alkanes. Originally, the term *aromatic* was used to describe this class of compounds because they were particularly fragrant. However, in modern chemistry the term *aromatic* denotes the presence of a six-membered ring that imparts different and unique properties to a molecule.

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:

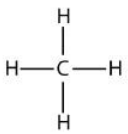


Figure 5.11.1 - Three-Dimensional Representation of Methane.

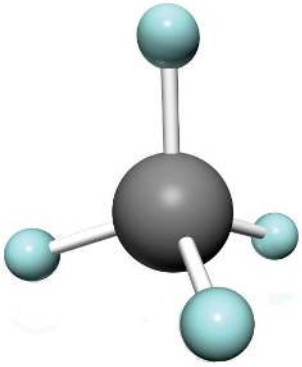
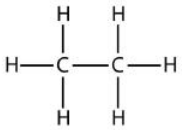
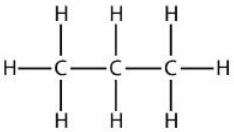


Figure 5.11.1 Three-Dimensional Representation of Methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron.

The next-largest alkane has two C atoms that are covalently bonded to each other. For each C atom to make four covalent bonds, each C atom must be bonded to three H atoms. The resulting molecule, whose formula is C_2H_6, is ethane:



Propane has a backbone of three C atoms surrounded by H atoms. You should be able to verify that the molecular formula for propane is C_3H_8:



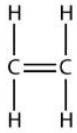
The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule. For example, the condensed structural formula for ethane is CH_3CH_3, while for propane it is $CH_3CH_2CH_3$. Table 5.11.1 - The First 10 Alkanes, gives the molecular formulas, the condensed structural formulas, and the names of the first 10 alkanes.

Table 5.11.1 The First 10 Alkanes

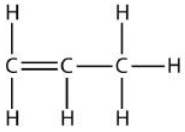
Molecular Formula	Condensed Structural Formula	Name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane

Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Alkenes have a C–C double bond. Because they have less than the maximum number of H atoms possible, they are **unsaturated hydrocarbons**. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:

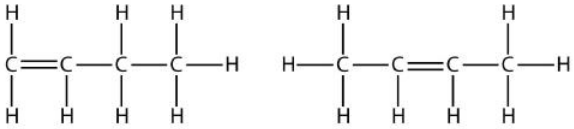


The next largest alkene—propene—has three C atoms with a C–C double bond between two of the C atoms. It is also known as propylene:



What do you notice about the names of alkanes and alkenes? The names of alkenes are the same as their corresponding alkanes except that the ending is *-ene*, rather than *-ane*. Using a stem to indicate the number of C atoms in a molecule and an ending to represent the type of organic compound is common in organic chemistry, as we shall see.

With the introduction of the next alkene, butene, we begin to see a major issue with organic molecules: choices. With four C atoms, the C–C double bond can go between the first and second C atoms or between the second and third C atoms:



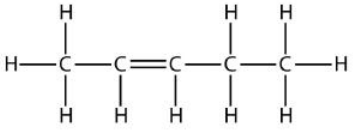
2 structural formulas for butene, with the first butene having the double bond on the first and second carbon from the left and the latter having its double bond on the second and third carbon from the left.

(A double bond between the third and fourth C atoms is the same as having it between the first and second C atoms, only flipped over.) The rules of naming in organic chemistry require that these two substances have different names. The first molecule is named *1-butene*, while the second molecule is named *2-butene*. The number at the beginning of the name indicates where the double bond originates. The lowest possible number is used to number a feature in a molecule; hence, calling the second molecule 3-butene would be incorrect. Numbers are common parts of organic chemical names because they indicate which C atom in a chain contains a distinguishing feature.

The compounds 1-butene and 2-butene have different physical and chemical properties, even though they have the same molecular formula—C_4H_8. Different molecules with the same molecular formula are called **isomers**. Isomers are common in organic chemistry and contribute to its complexity.

Example 5.11.1

Based on the names for the butene molecules, propose a name for this molecule.



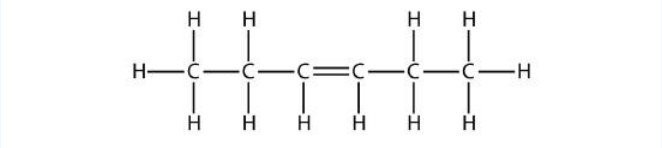
A structural formula of a five carbon molecule with a double bond on the third and fourth carbon from the left. There are ten hydrogen atoms in total.

Solution

With five C atoms, we will use the *pent-* stem, and with a C–C double bond, this is an alkene, so this molecule is a pentene. In numbering the C atoms, we use the number *2* because it is the lower possible label. So this molecule is named 2-pentene.

? Exercise 5.11.1

Based on the names for the butene molecules, propose a name for this molecule.



A structural formula of a six carbon molecule with a double bond on the third and fourth carbon from the left. There are twelve hydrogen atoms in total.

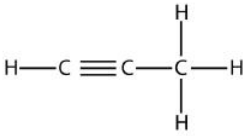
Answer

3-hexene

Alkynes, with a C–C triple bond, are named similarly to alkenes except their names end in *-yne*. The smallest alkyne is ethyne, which is also known as acetylene:

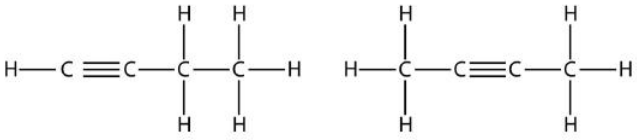


Propyne has the structure



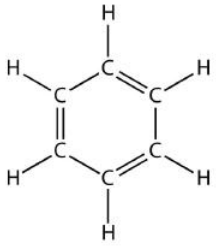
Structural formula showing three carbon molecules with a triple bond present between the first and second carbon atom. The appropriate number of hydrogen atoms is attached to each carbon atom.

With butyne, we need to start numbering the position of the triple bond, just as we did with alkenes:



Two structural formula of butyne. One butyne has a triple bond between the first and second carbon atom, while two butyne has the triple bond between the second and third carbon atom.

Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



The six carbons are arranged in a hexagon pattern with one hydrogen atom emerging outwards from each carbon atom. The presence of a double bond is alternated between every other carbon atom.

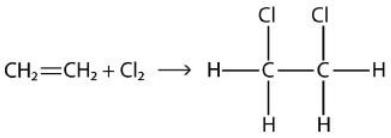
The alternating single and double C–C bonds give the benzene ring a special stability, and it does not react like an alkene as might be suspected. Benzene has the molecular formula C_6H_6; in larger aromatic compounds, a different atom replaces one or more of the H atoms.

As fundamental as hydrocarbons are to organic chemistry, their properties and chemical reactions are rather mundane. Most hydrocarbons are nonpolar because of the close electronegativities of the C and H atoms. As such, they dissolve only sparingly in H_2O and other polar solvents. Small hydrocarbons, such as methane and ethane, are gases at room temperature, while larger hydrocarbons, such as hexane and octane, are liquids. Even larger hydrocarbons are solids at room temperature and have a soft, waxy consistency.

Hydrocarbons are rather unreactive, but they do participate in some classic chemical reactions. One common reaction is substitution with a halogen atom by combining a hydrocarbon with an elemental halogen. Light is sometimes used to promote the reaction, such as this one between methane and chlorine:

$$CH_4 + Cl_2 \overset{light}{\rightarrow} CH_3Cl + HCl$$

Halogens can also react with alkenes and alkynes, but the reaction is different. In these cases, the halogen reacts with the C–C double or triple bond and inserts itself onto each C atom involved in the multiple bonds. This reaction is called an **addition reaction**. One example is



Structural formula showing the reaction of ethylene with a chlorine molecule to form ethylene dichloride.

The reaction conditions are usually mild; in many cases, the halogen reacts spontaneously with an alkene or an alkyne.

Hydrogen can also be added across a multiple bond; this reaction is called a **hydrogenation reaction**. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed at a reasonable pace:

$$CH_2 = CH_2 + H_2 \overset{metal\ catalyst}{\rightarrow} CH_3CH_3$$

By far the most common reaction of hydrocarbons is **combustion**, which is the combination of a hydrocarbon with O_2 to make CO_2 and H_2O. The combustion of hydrocarbons is accompanied by a release of energy and is a primary source of energy production in our society (Figure 5.11.2 - Combustion). The combustion reaction for gasoline, for example, which can be represented by C_8H_{18}, is as follows:

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O + \sim 5060kJ$$



Figure 5.11.2 Combustion © Thinkstock. The combustion of hydrocarbons is a primary source of energy in our society.

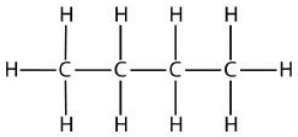
Key Takeaways

- The simplest organic compounds are hydrocarbons and are composed of carbon and hydrogen.
- Hydrocarbons can be aliphatic or aromatic; aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes.
- The combustion of hydrocarbons is a primary source of energy for our society.

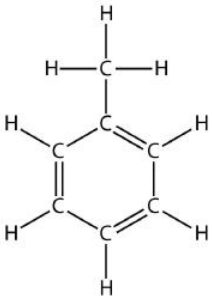
? Exercise 5.11.2

1. Define *hydrocarbon*. What are the two general types of hydrocarbons?
2. What are the three different types of aliphatic hydrocarbons? How are they defined?
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

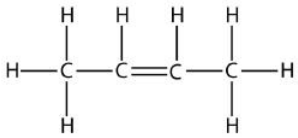
a.



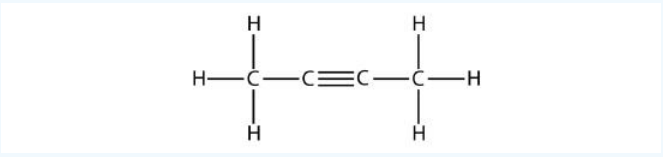
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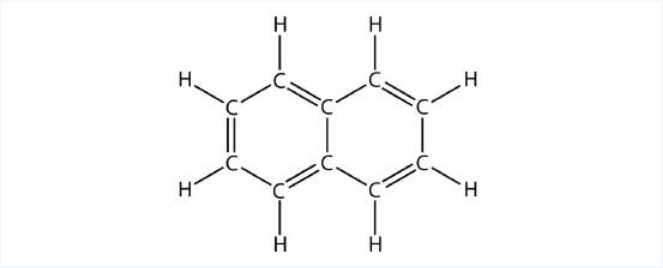


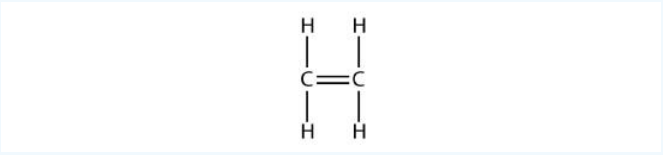
c.



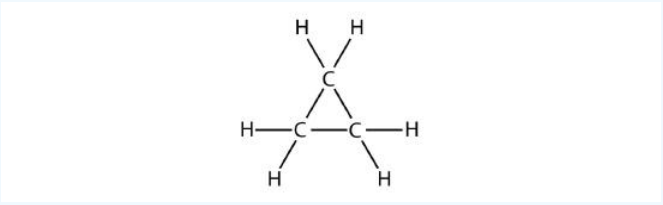
4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

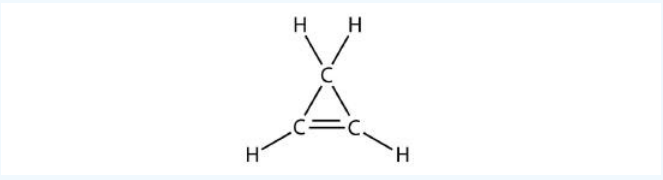
a. 

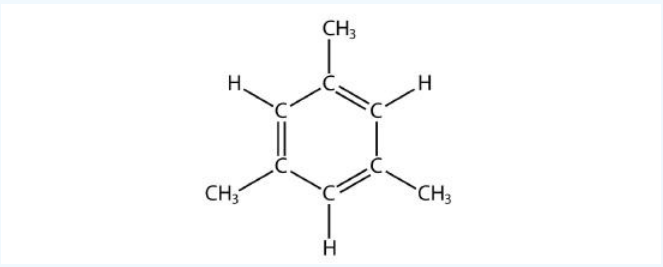
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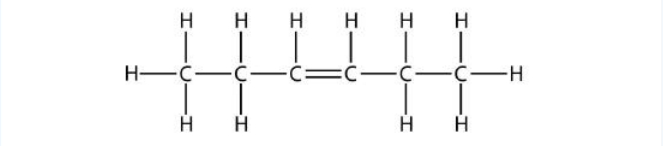
5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

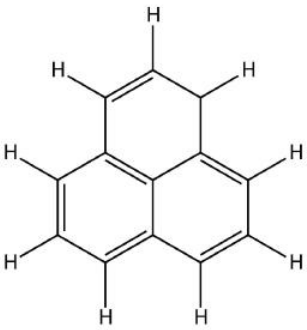
a. 

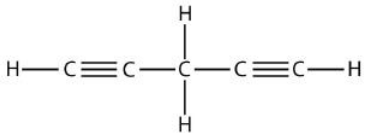
b. 

c. 

6. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

b. 

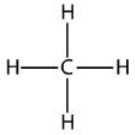
c. 

7. Name and draw the structural formulas for the four smallest alkanes.
8. Name and draw the structural formulas for the four smallest alkenes.
9. What does the term *aromatic* imply about an organic molecule?
10. What does the term *normal* imply when used for alkanes?
11. Explain why the name *1-propene* is incorrect. What is the proper name for this molecule?
12. Explain why the name *3-butene* is incorrect. What is the proper name for this molecule?
13. Name and draw the structural formula of each isomer of pentene.
14. Name and draw the structural formula of each isomer of hexyne.
15. Write a chemical equation for the reaction between methane and bromine.
16. Write a chemical equation for the reaction between ethane and chlorine.
17. Draw the structure of the product of the reaction of bromine with propene.
18. Draw the structure of the product of the reaction of chlorine with 2-butene.
19. Draw the structure of the product of the reaction of hydrogen with 1-butene.
20. Draw the structure of the product of the reaction of hydrogen with 1-butene.
21. Write the balanced chemical equation for the combustion of heptane.
22. Write the balanced chemical equation for the combustion of nonane.

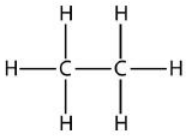
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Answers

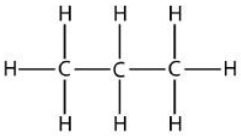
1. an organic compound composed of only carbon and hydrogen; aliphatic hydrocarbons and aromatic hydrocarbons
2.
3. a. aliphatic; alkane
   b. aromatic
   c. aliphatic; alkene
4.
5. a. aliphatic; alkane
   b. aliphatic; alkene
   c. aromatic
6.



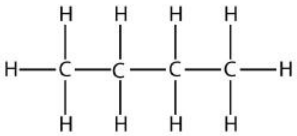
Methane



Ethane

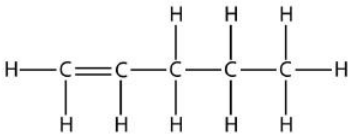


Propane

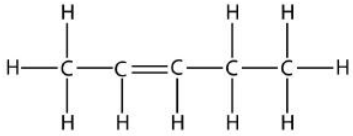


Butane

7.
8.
9. Aromatic means that the molecule has a benzene ring.
10.
11. The 1 is not necessary. The name of the compound is simply *propene*.
12.

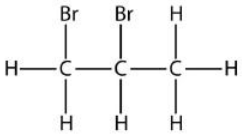


1-Pentene

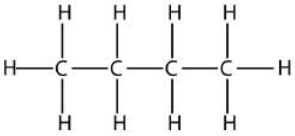


2-Pentene

13.
14.
15. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$
16.



17.
18.



19.
20.
21. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

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CHAPTER OVERVIEW

6: Chemical Bonding I- Drawing Lewis Structures and Determining Molecular Shapes

6.1: Morphine - A Molecular Imposter

6.2: Electronegativity and Bond Polarity

6.3: Writing Lewis Structures for Molecular Compounds and Polyatomic Ions

6.4: Resonance and Formal Charge

6.5: Exceptions to the Octet Rule- Odd-Electron Species, Incomplete Octets, and Expanded Octets

6.6: Bond Energies and Bond Lengths

6.7: VSEPR Theory - The Five Basic Shapes

6.8: VSPER Theory- The Effect of Lone Pairs

6.9: VSPER Theory - Predicting Molecular Geometries

6.10: Molecular Shape and Polarity

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6.1: Morphine - A Molecular Imposter



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6.2: Electronegativity and Bond Polarity

Learning Objectives

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the bonding electron pair is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. As demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity** (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.*

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

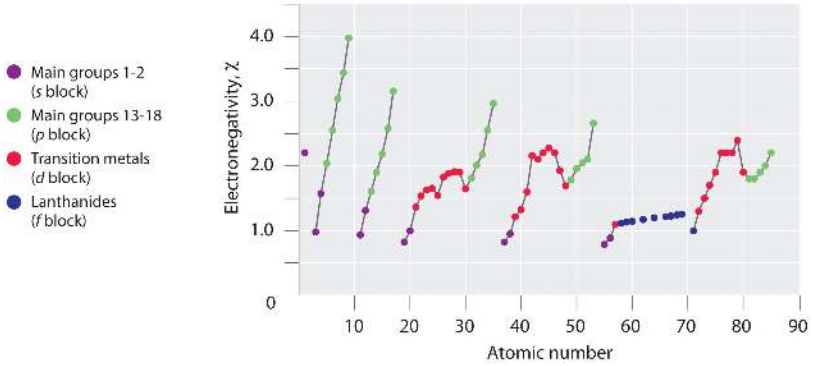
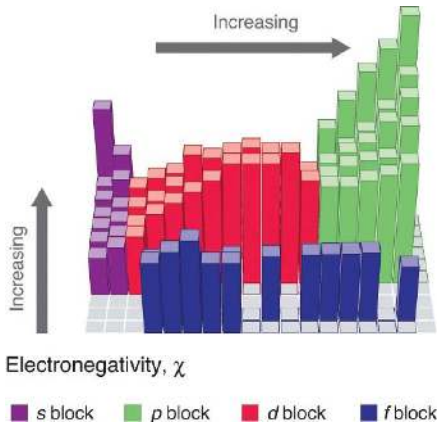


Figure 6.2.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table
The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations in Pauling's electronegativity values are illustrated in Figures 6.2.1 and 6.2.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

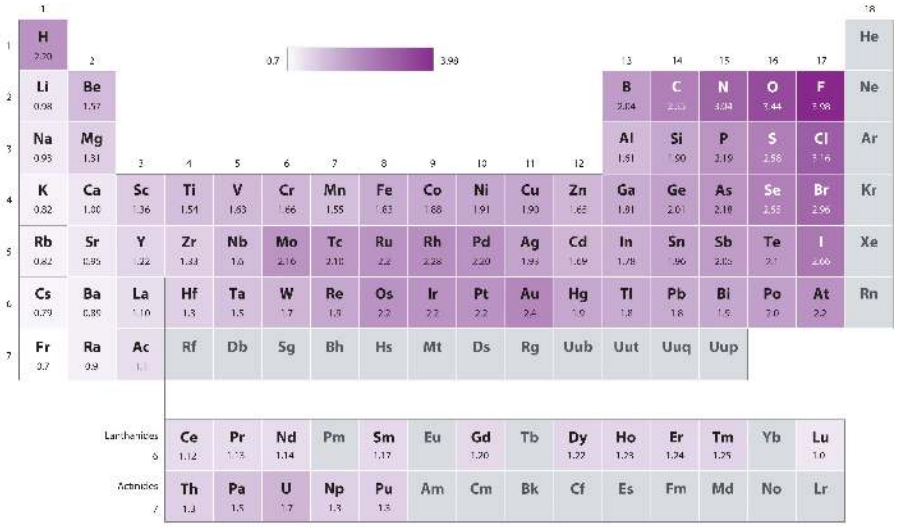


The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

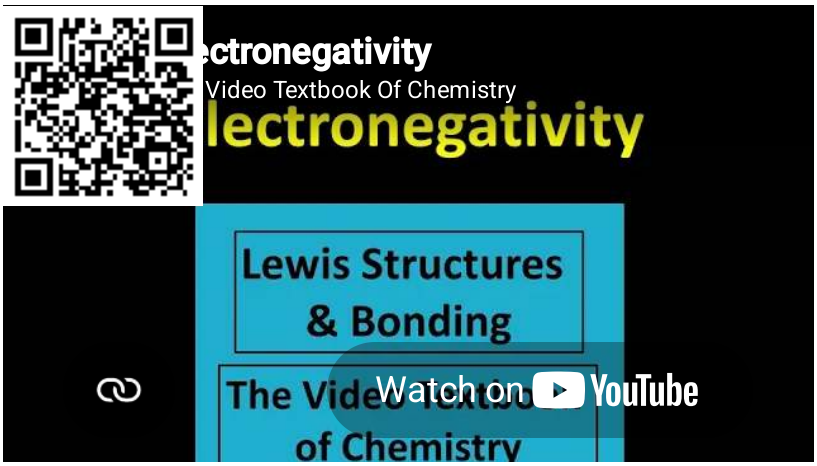
Figure 6.2.2***:*** *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school, but was later denied a high school degree, and had to work several jobs to put himself through college. Pauling would go on to become one of the most influential chemists of the century if not all time. He won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962.



Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem, e.g., the Mulliken, Allred-Rochow, and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.



Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$ in Figure 6.2.2) 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 **metalloids** (or semimetals), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 6.2.3 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

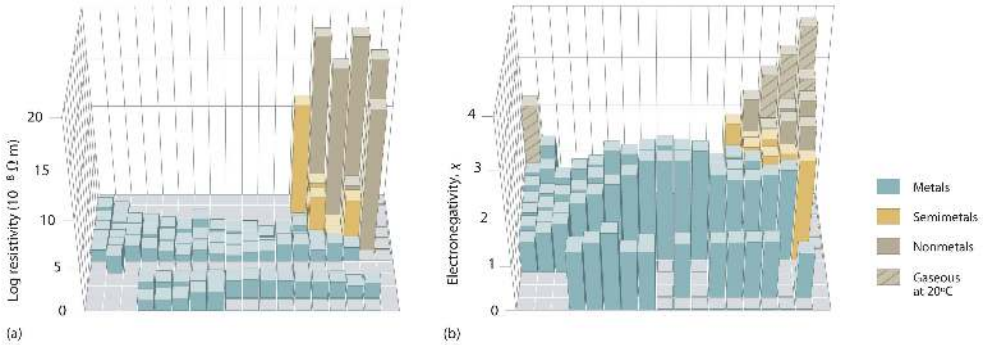


Figure 6.2.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Metals are blue, semimetals are yellow, nonmetals are gray, gaseous at 20 degrees C are gray with dashed lines.

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states(opens in new window) are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

✔ Example 6.2.1: Increasing Electronegativity

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a metalloid according to its location about the diagonal belt of metalloids running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 8.4.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of metalloids running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a metalloid, and Se and Cl are nonmetals.

? Exercise 6.2.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Answer

Rb < Zr < Ge < N < O; metals (Rb, Zr); metalloid (Ge); nonmetal (N, O)

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 6.2.4 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.

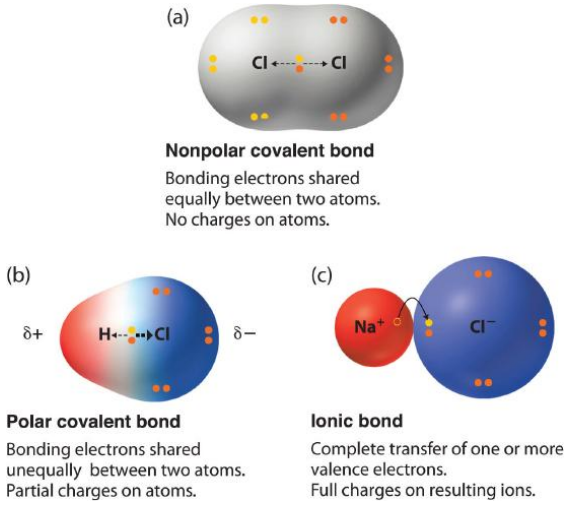


Figure 6.2.4: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{\text{less electronegative}}{A}} - \underset{\delta^-}{\overset{\text{more electronegative}}{B}} \tag{6.2.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: χ_{Cl} = 3.16, χ_H = 2.20, and χ_{Na} = 0.93. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character **increase** with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge *Q* on the bonded atoms and the distance *r* between the partial charges:

$$\mu = Qr \tag{6.2.2}$$

where *Q* is measured in coulombs (C) and *r* in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{6.2.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 6.2.4).

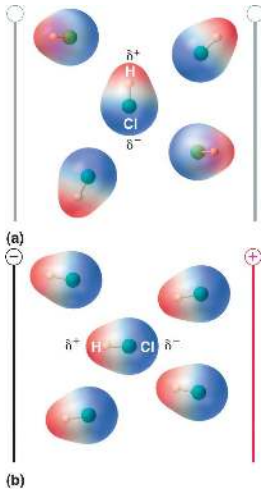


Figure 6.2.5: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field. In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive 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 6.2.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$\begin{aligned} Q = \frac{\mu}{r} &= 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) \\ &= 2.901 \times 10^{-20}\ C \end{aligned} \tag{6.2.4}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20} \cancel{C}}{1.6022 \times 10^{-19} \cancel{C}} = 0.1811\ e^- \tag{6.2.5}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^+}{H} - \overset{0.18\delta^-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), 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 6.2.6 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 6.2.6 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 6.2.2.

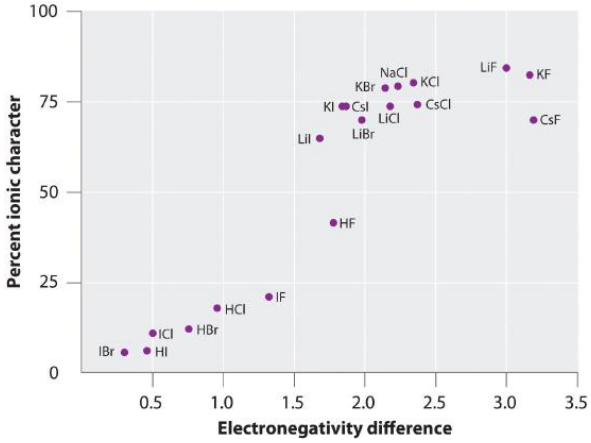


Figure 6.2.6: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 6.2.2

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 6.2.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r}$$

$$= 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\%\ ionic\ character = \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\%$$

? Exercise 6.2.2

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%

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

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6.3: Writing Lewis Structures for Molecular Compounds and Polyatomic Ions

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 6.3.1):

- The electrons in the two atoms repel each other because they have the same charge (
- *The electrons in the two atoms repel each other because they have the same charge (E > 0).*
- *Similarly, the protons in adjacent atoms repel each other (E > 0).*
- *The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa (E < 0). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.*

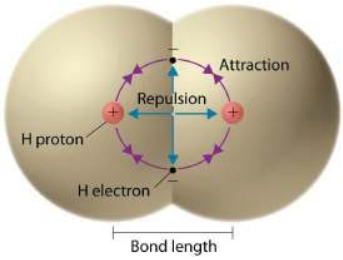


Figure 6.3.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 6.3.2) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures 6.3.1 and 6.3.2, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

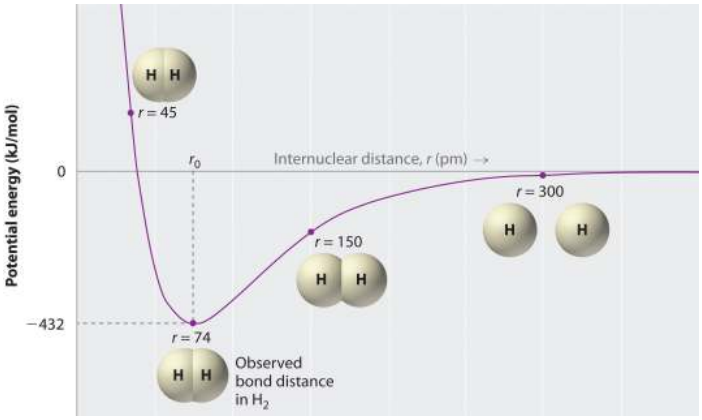


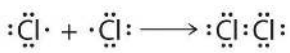
Figure 6.3.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the

internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

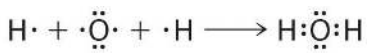
Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:

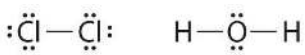


Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.

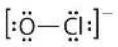
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

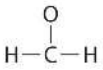
The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



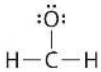
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

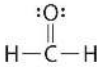
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 6.3.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

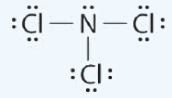
Asked for: Lewis electron structures

Strategy:

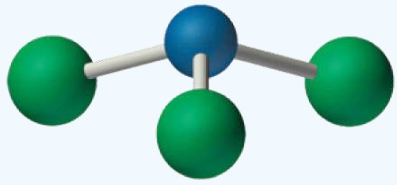
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

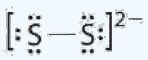


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

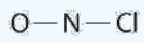


Nitrogen trichloride

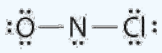
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



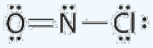
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



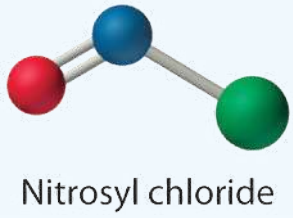
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



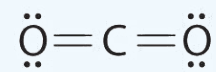
All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



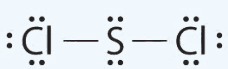
? Exercise 6.3.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

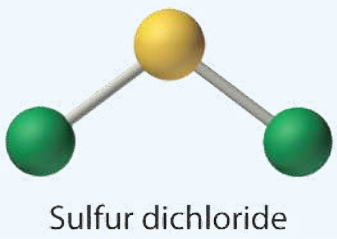
Answer

1. 



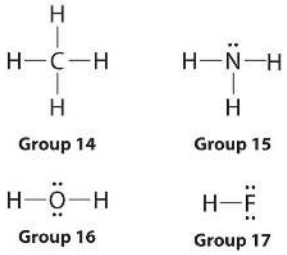
2. 

Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.

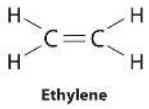


Using Lewis Electron Structures to Explain Stoichiometry

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group 17 (the halogens), this number is one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

> Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 6.3.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

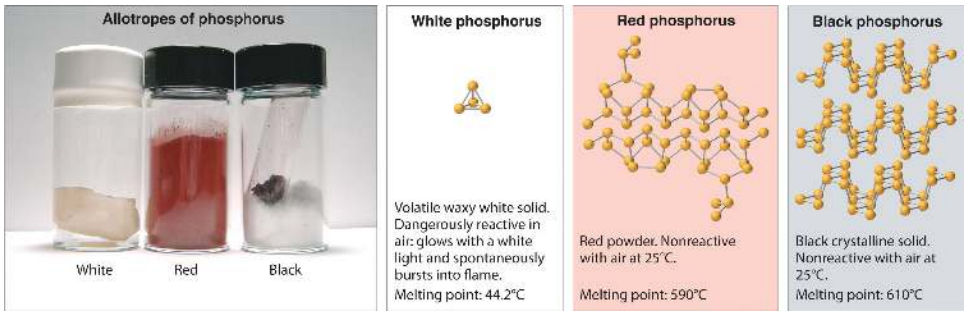


Figure 6.3.3: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus 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.

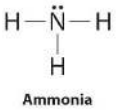
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- 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 6.3.1, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{6.3.1}$$

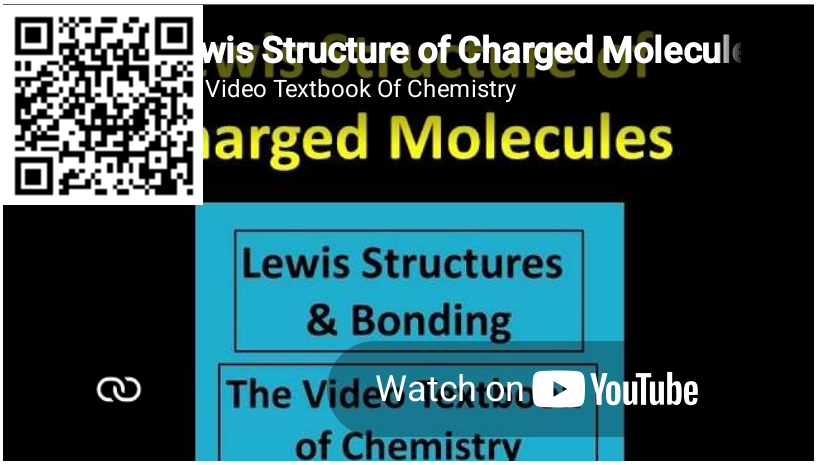
A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 6.3.1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{6.3.2}$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

> An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.



Example 6.3.2: The Ammonium Ion

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

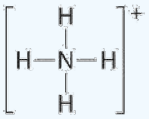
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 6.3.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The central nitrogen is bonded to four hydrogens. The molecule is surrounded by square brackets. Outside the bracket is where the positive charge is placed.

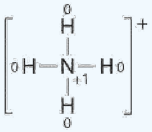
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ???, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus



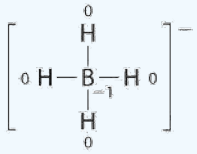
In the Lewis structure, each hydrogen has a zero placed nearby while the nitrogen has a +1 placed nearby.

Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 6.3.2

Write the formal charges on all atoms in BH_4^-.

Answer



Four hydrogens are bonded to a central boron. Each hydrogen has a zero placed nearby while the boron has a -1. The molecule is surrounded by square brackets. Outside of the brackets is a negative charge.

If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

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6.4: Resonance and Formal Charge

Learning Objectives

- To understand the concept of resonance.

Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integral number of covalent bonds.

Sometimes one Lewis Structure is not Enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



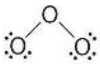
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



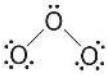
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

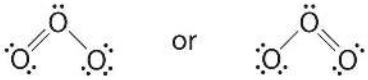


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

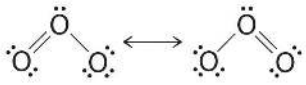


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



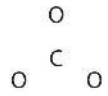
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:



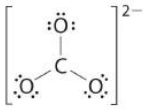
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:



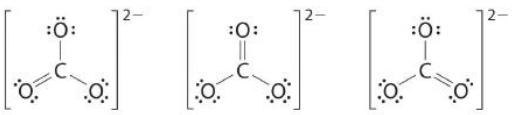
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



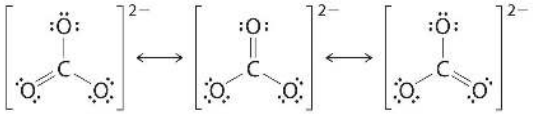
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



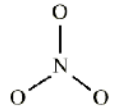
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

The actual structure is an average of these three resonance structures.

The Nitrate (NO_3^-) ion

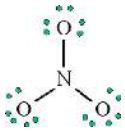
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

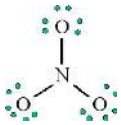


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

3. Add octet electrons to the atoms bonded to the center atom:

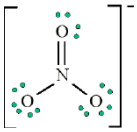


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

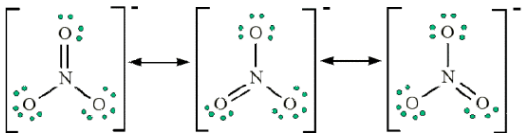
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



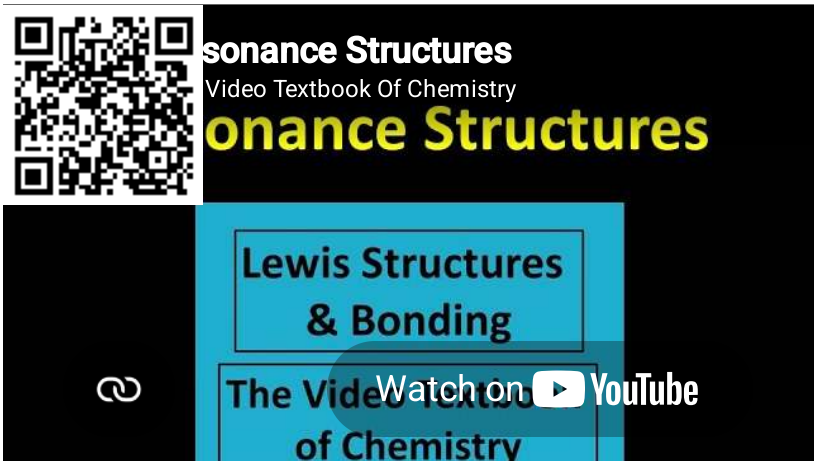
A double bond is added between one oxygen and the central nitrogen. The molecule has a negative charge.

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond.



Example 6.4.1: 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:

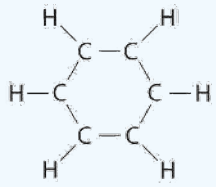
A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

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.

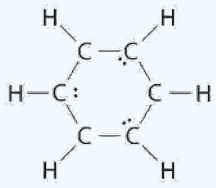
Solution:

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.

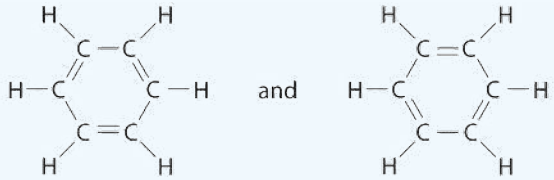
B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:



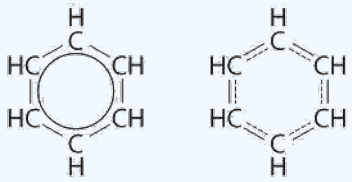
Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of

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:

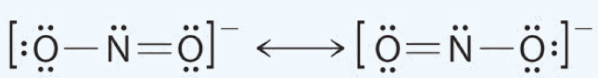


Benzene

? Exercise 6.4.1: Nitrite Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



There is a double bond between one oxygen and the nitrogen, It can be found on the left oxygen or the right oxygen.

Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example 6.4.1. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance

structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

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6.5: Exceptions to the Octet Rule- Odd-Electron Species, Incomplete Octets, and Expanded Octets

Learning Objectives

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be Nitrogen (II) Oxide also called nitric oxide (NO. Nitrogen has 5 valence electrons while Oxygen has 6. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in.*

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitric oxide. nitric oxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitric oxide had ten valence electrons we would come up with the Lewis Structure (Figure 6.5.1):

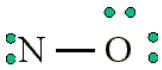


Figure 6.5.1: This is if nitric oxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure 6.5.2 based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure 6.5.1, 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 6.5.1, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitric oxide (Figure 6.5.2):

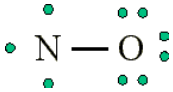


Figure 6.5.2: The proper Lewis structure for NO molecule

Free Radicals

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call Free Radicals. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the

gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, an odd Number of Valence Electrons will result in the molecule being paramagnetic.

Exception 2: Incomplete Octets

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one were to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure 6.5.2):

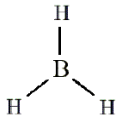


Figure 6.5.3: The structure of BH_3 is square planer.

The problem with this structure is that boron has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3, the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure 6.5.4).

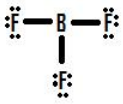


Figure 6.5.4

If you look Figure 6.5.4, 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 6.5.5):

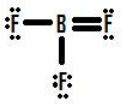


Figure 6.5.5

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 6.5.5, 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 6.5.6:

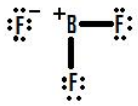


Figure 6.5.6

A bond is broken between one of the fluorine's and the boron making the free fluorine negatively charged and the boron positively charged.

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a resonance of all three structures: the one with the incomplete octet (Figure 6.5.4), the one with the double bond (Figure 6.5.5), and the one with the ionic bond (Figure 6.5.6). The most contributing structure is probably the incomplete octet structure (due to Figure 6.5.5 being basically impossible and Figure 6.5.6 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 .

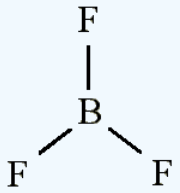
Example 6.5.1: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

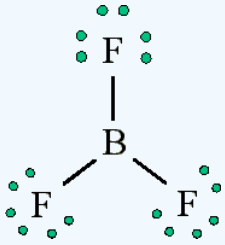
Solution

1. Add electrons (3*7) + 3 = **24**

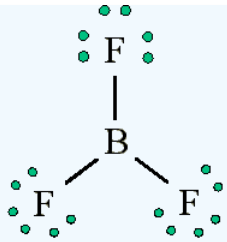
2. Draw connectivities:



3. Add octets to outer atoms:

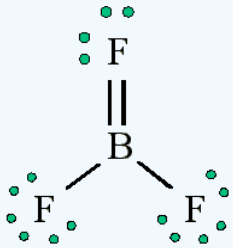


4. Add extra electrons (24-24=0) to central atom:



5. Does central electron have octet?

- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:

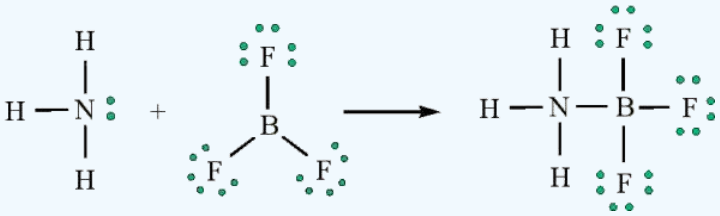


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

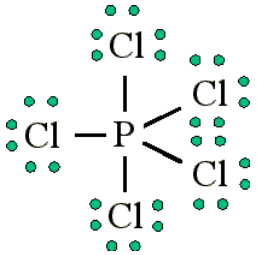
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



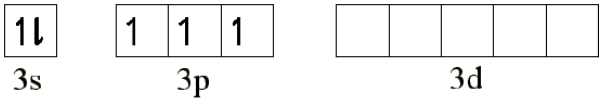
Exception 3: Expanded Valence Shells

More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below*, which those terminal atoms bond to. For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available n*s* 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:

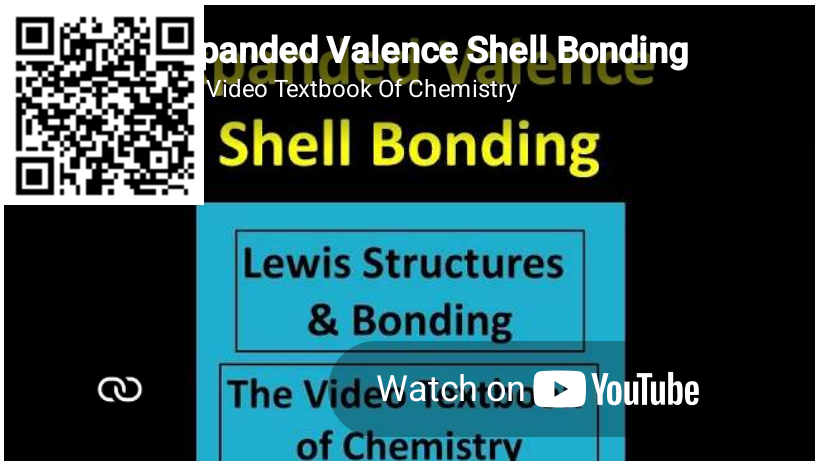


Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- 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 6.5.2: 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:

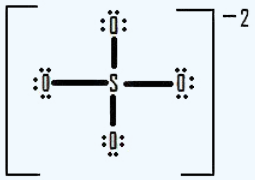


Figure 6.5.12

Four oxygens are bonded to a central sulfur. Each oxygen has 3 lone pairs. The molecule has a minus 2 charge.

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygens in this structure has a formal charge of -1. Sulfur has

four electrons around it in this structure (one from each of its four bonds) which is two electrons more than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

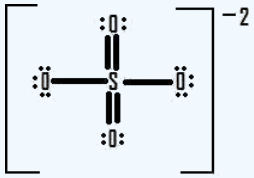


Figure 6.5.13

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 6.5.12, as opposed to +2 and -1 (difference of 3) in Figure 6.5.12) 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.

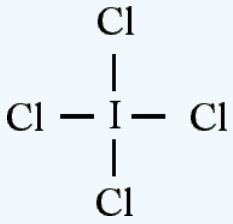
Example 6.5.3: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

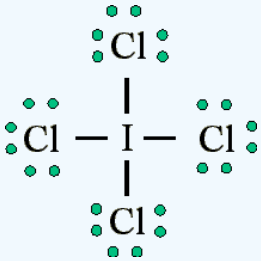
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

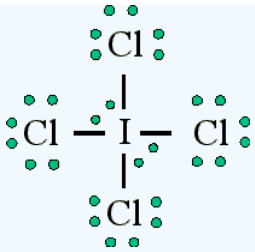
2. Draw the connectivities:



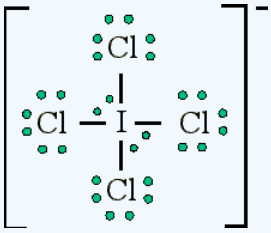
3. Add octet of electrons to outer atoms:



4. Add extra electrons (36-32=**4**) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)



Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.

Summary

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

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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.

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6.6: Bond Energies and Bond Lengths

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 6.6.1 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table 6.6.1: 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

$$\mathrm{Cl{-}Cl} > \mathrm{Br{-}Br} > \mathrm{F{-}F} > \mathrm{I{-}I}$$

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.

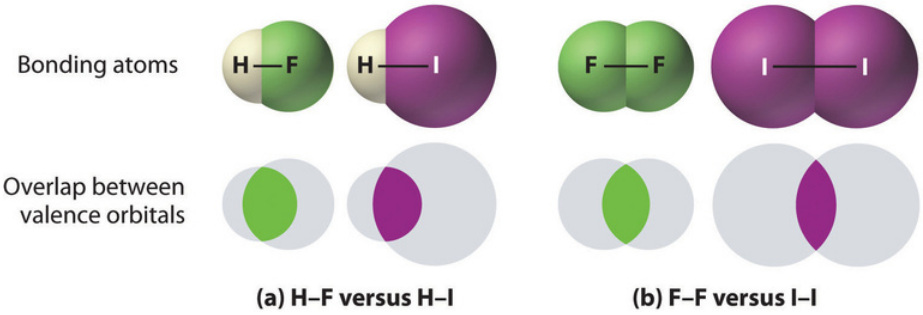


Figure 6.6.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) 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 6.6.2); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 6.6.1 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 6.6.2: 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
$CH_3(g) \rightarrow CH_2(g) + H(g)$	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 ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \tag{6.6.1}$$

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:

$$CH_3(CH_2)_5CH_3\,(l) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g) \tag{6.6.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Binds Broken (kJ/mol) and Bonds Formed (kJ/mol)

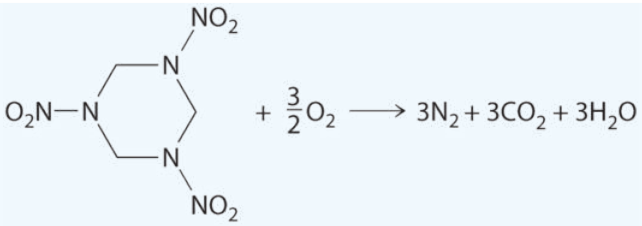
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately −4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f^o values ($\Delta H_{rxn} = -481\ 7 kJ/mol$), 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 6.6.1: 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 6.6.1 to estimate the ΔH_{rxn} per mole of RDX.



RDX

Given: chemical reaction, structure of reactant, and Table 6.6.1.

Asked for: ΔH_{rxn} per mole

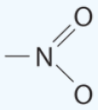
Strategy:

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 6.6.1 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		

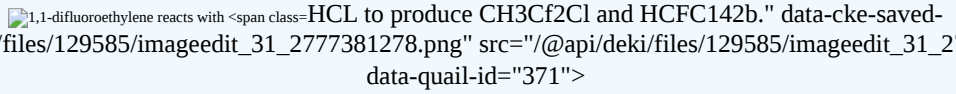
B From Equation 6.6.1, we have

$$\begin{aligned}\Delta H_{rxn} &\approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \\ &= 7962\ kJ/mol - 10,374\ kJ/mol \\ &= -2412\ kJ/mol\end{aligned}$$

Thus this reaction is also highly exothermic

Exercise 6.6.1: Freon

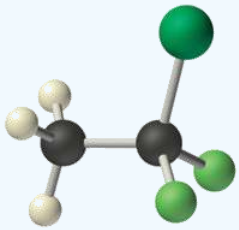
The molecule HCFC-142b is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons and can be prepared by adding HCl to 1,1-difluoroethylene:



Use tabulated bond energies to calculate ΔH_{rxn}.

Answer

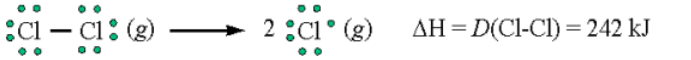
−54 kJ/mol



HCFC-142b

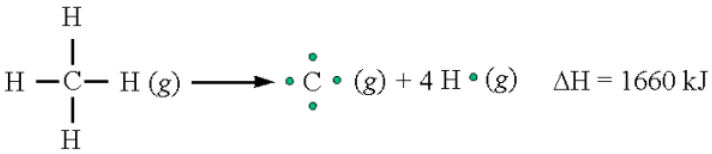
Bond Dissociation Energy

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 bonc

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:

$$D(C-H) = (1660/4)\, kJ/mol$$
$$= 415\, kJ/mol$$

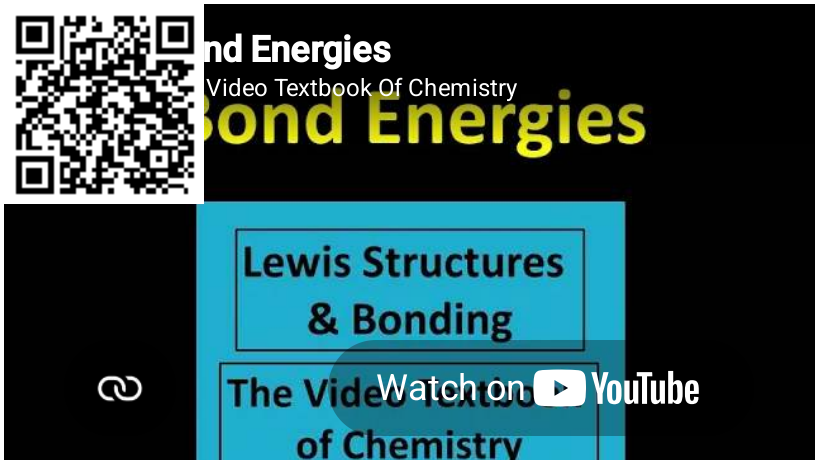
The bond energy for a given bond is influenced by the rest of the molecule. However, this is a relatively small effect (suggesting that bonding electrons are localized between the bonding atoms). Thus, the bond energy for most bonds varies little from the average bonding energy for that type of bond

Bond energy is always a *positive* value - it takes energy to break a covalent bond (conversely energy is released during bond formation)

Table 6.6.4: 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.



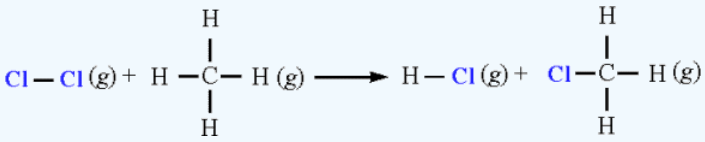
Bond Energies and the Enthalpy of Reactions

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:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \tag{6.6.3}$$

Example 6.6.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation 6.6.3, 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

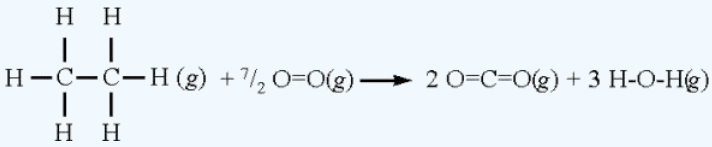
$$\begin{aligned}\Delta H &= [D(Cl-Cl)+D(C-H)]-[D(H-Cl)+D(C-Cl)]\\ &= [242kJ+413kJ]-[431kJ+328kJ]\\ &= -104\,kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example 6.6.3: 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 6.6.3, 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 6.6.5: 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.

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6.7: VSEPR Theory - The Five Basic Shapes

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.

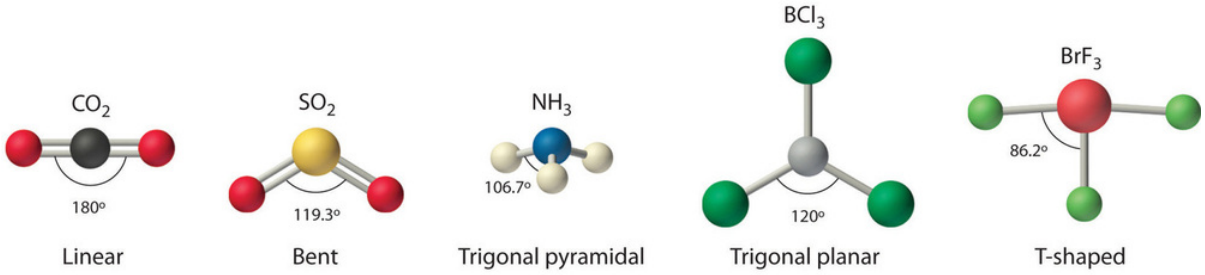


Figure 6.7.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

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 6.7.1 and 6.7.2.

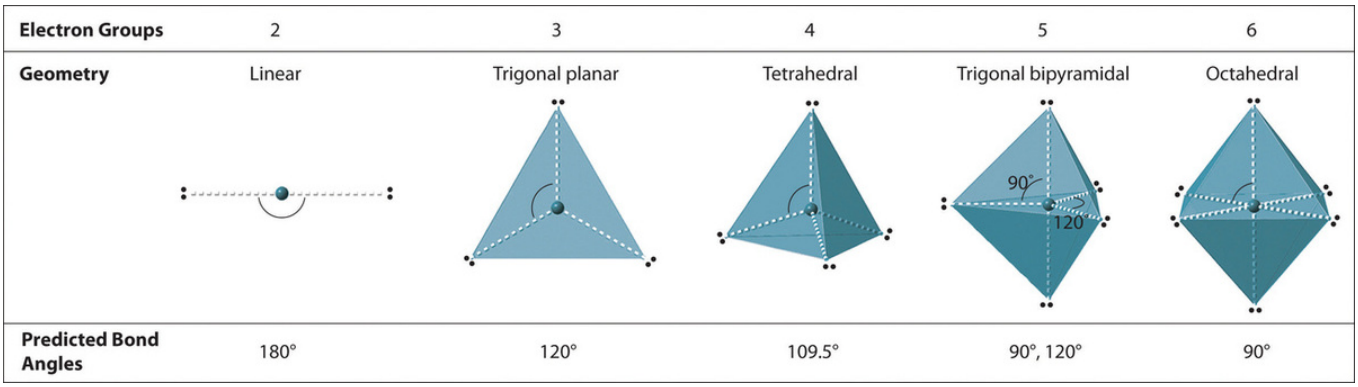


Figure 6.7.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

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 6.7.2 and Figure 6.7.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

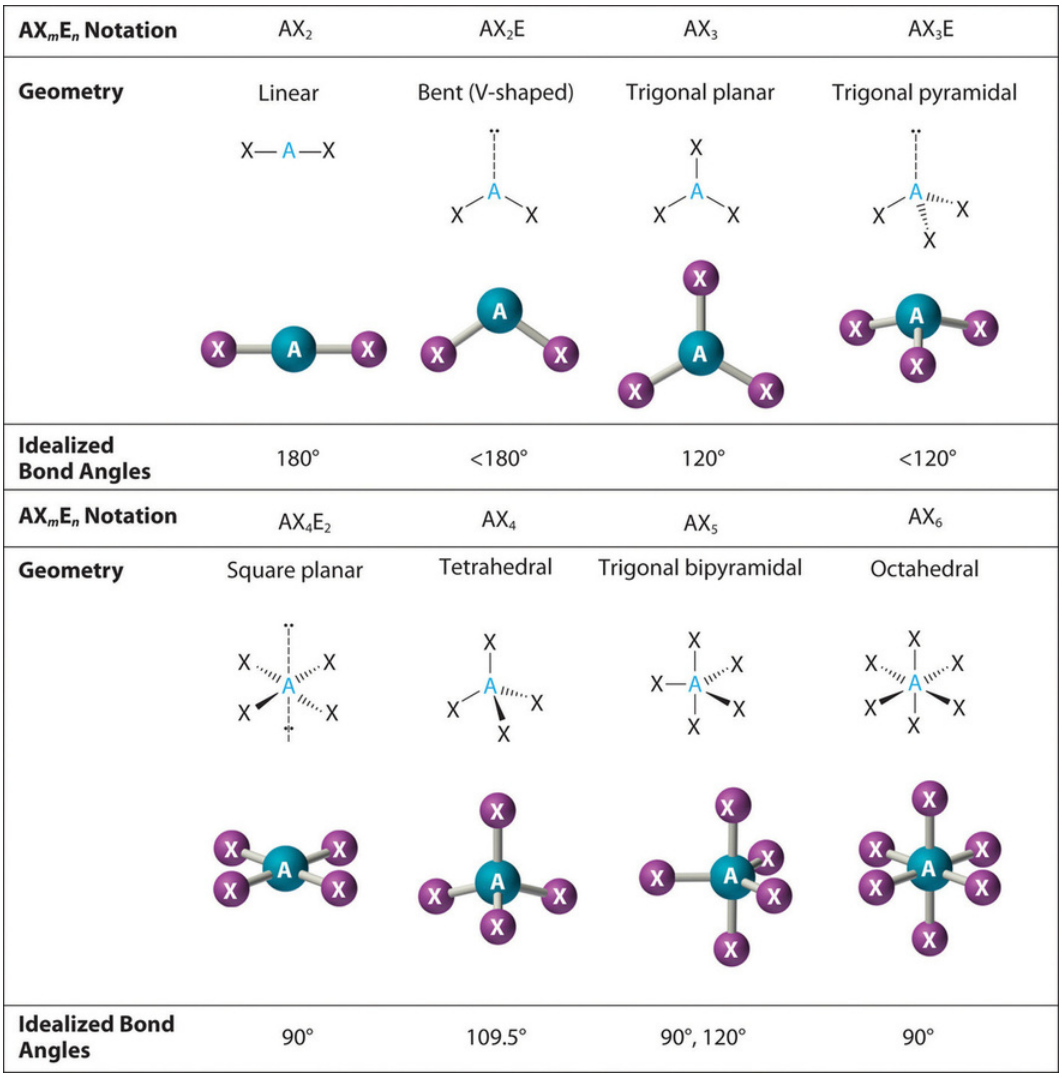


Figure 6.7.3: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

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

H:Be:H or H—Be—H

Lewis structure

Figure 6.7.2 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 6.7.3 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.

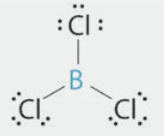
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

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 6.7.3). The structure of CO_2 is shown in Figure 6.7.1.

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

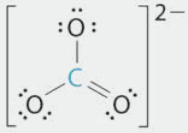
Figure 6.7.2): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 6.7.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 6.7.2.

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



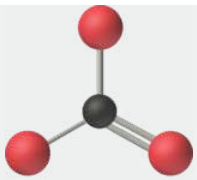
Lewis structure

Figure 6.7.2).

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 6.7.3 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.

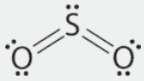


Figure 6.7.2): (CC BY-NC-SA; anonymous)

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 6.7.4). 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 6.7.2 and 6.7.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

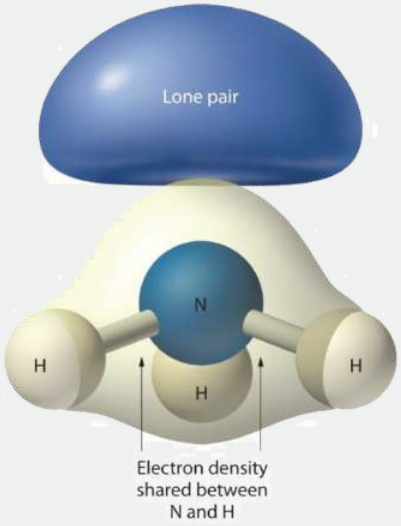
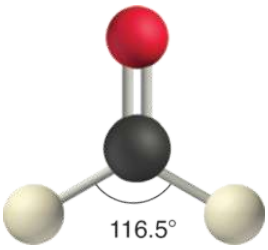


Figure 6.7.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

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°).

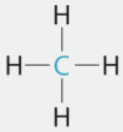


Four Electron Groups

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

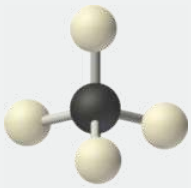


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 6.7.2, 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.

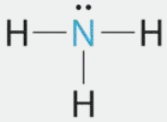
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 6.7.3).



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 6.7.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 6.7.3 and Figure 6.7.4).

AX_2E_2 Molecules: H_2O

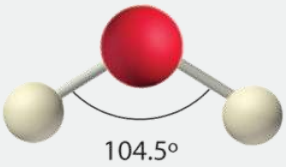
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



Figure 6.7.2: (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

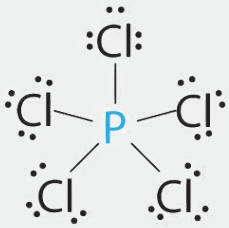
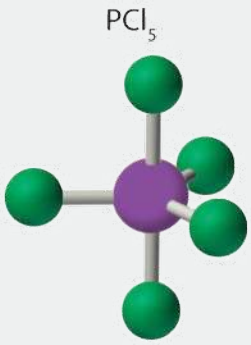


Figure 6.7.2): (CC BY-NC-SA; anonymous)

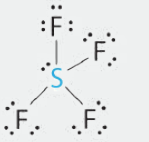
3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 6.7.3. 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 6.7.2.

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.

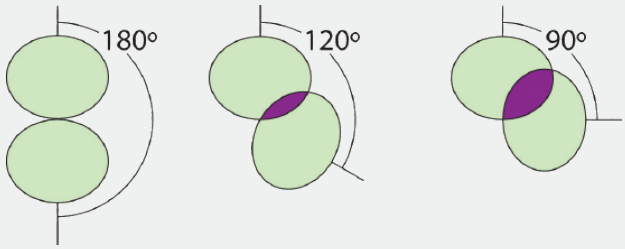
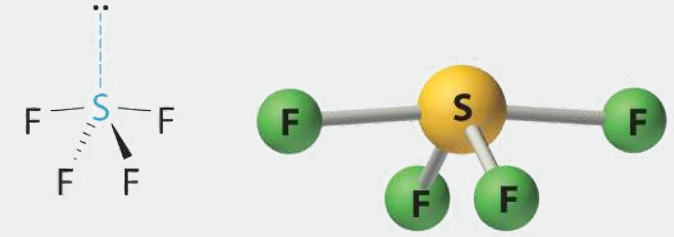


Figure 6.7.5: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

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.

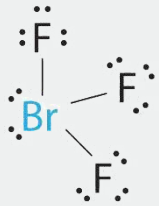
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



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			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

If the lone pairs are axiam, the 90 degree LP-LP interactions are o and the 90 degree LP-BP interaction is zero. If the Lone pares are equatorial there are zero 90 degree LP-LP interactions and four 90 degree LP-BP intereactions. If the lone pairs are axial and equatorial there is one 90 degree LP-LP interaction and three 90 degree LP-BP interaction.

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP

repulsions (Figure 6.7.2.1).

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.

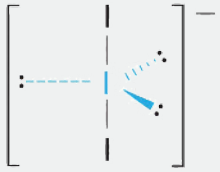
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



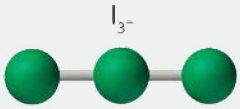
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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 6.7.2.)

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



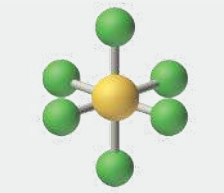
Lewis structure

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 6.7.2 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.

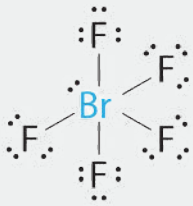
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



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

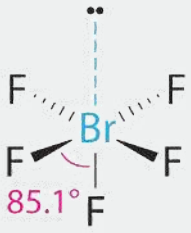


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

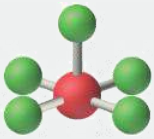
With its expanded valence, this species is an exception to the octet rule.

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.

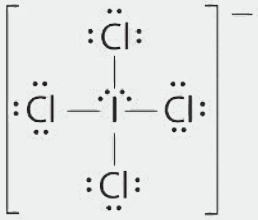
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



Molecular geometry
(square pyramidal)

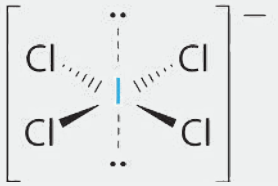
AX_4E_2 Molecules: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



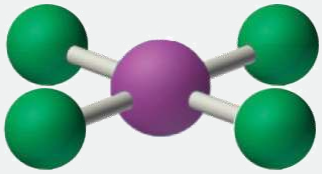
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

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 6.7.6.

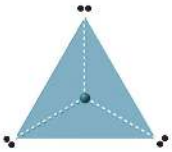
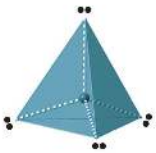
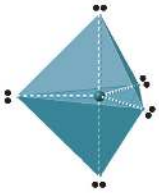
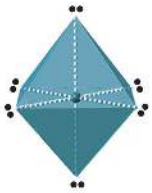
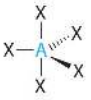
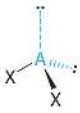
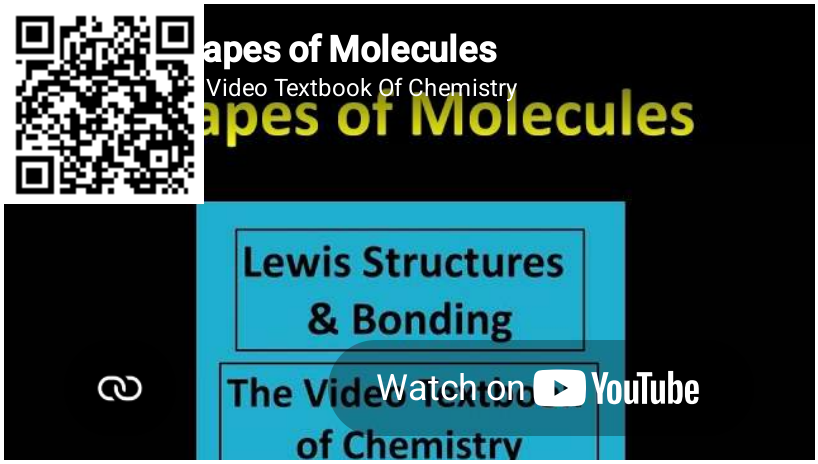
Electron Groups	2	3	4	5	6
Molecular Geometry					
	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Zero Lone Pairs					
	Linear AX_2	Trigonal planar AX_3	Tetrahedral AX_4	Trigonal bipyramidal AX_5	Octahedral AX_6
One Lone Pair					
		Bent (V-shaped) AX_2E	Trigonal pyramidal AX_3E	Seesaw AX_4E One axial lone pair	Square pyramidal AX_5E
Two Lone Pairs					
			Bent (V-shaped) AX_2E_2	T-shaped AX_3E_2 Two axial lone pairs	Square planar AX_4E_2
Three Lone Pairs					
				Linear AX_2E_3 Three axial lone pairs	

Figure 6.7.6***:*** *Overview of Molecular Geometries*



Example 6.7.1

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

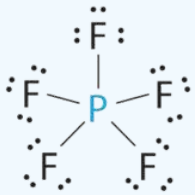


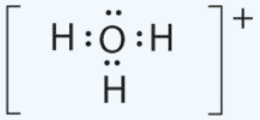
Figure 6.7.6): (CC BY-NC-SA; anonymous)

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

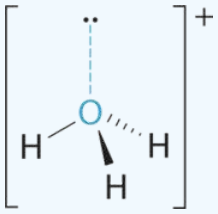


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

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 6.7.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

Example 6.7.2

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 Example6.7.1.

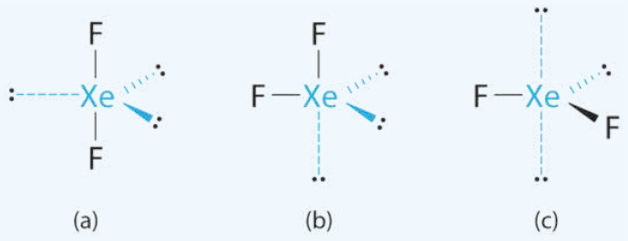
Solution:

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

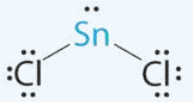
If the two F atoms are axial ther are zero 90 LP-LP interactions. If the two F atoms are axial and equatorial or just equatorial, there are 2 90 LP-LP interactions.

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 6.7.2

Predict the molecular geometry of each molecule.

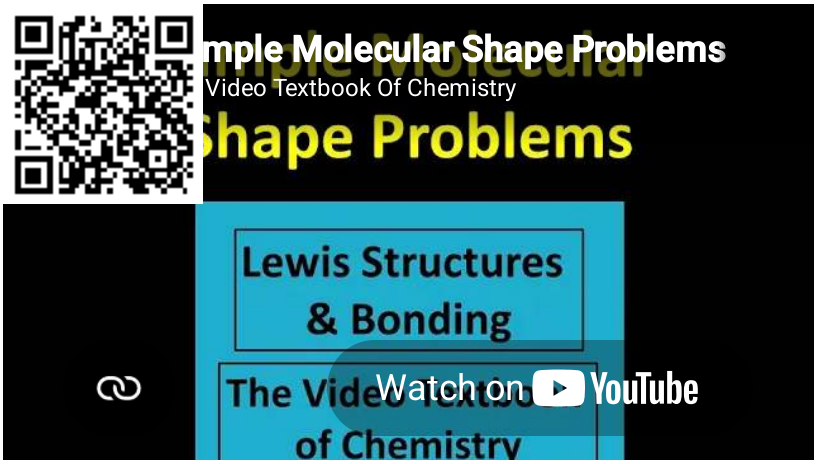
a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

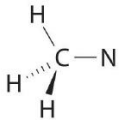


Molecules with No Single Central Atom

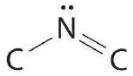
The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. 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:

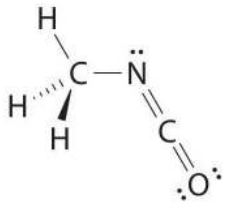


Figure 6.7.7).

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.

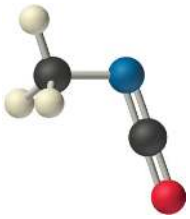


Figure 6.7.7: The Experimentally Determined Structure of Methyl Isocyanate

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 6.7.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), 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 6.7.3 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 6.7.3

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

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

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 6.7.8*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 6.7.8*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.

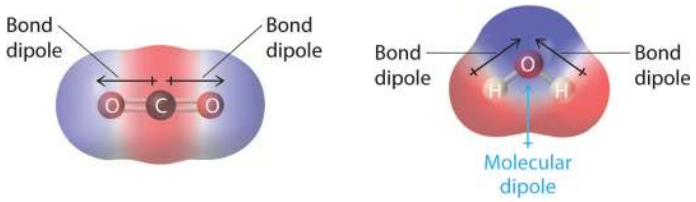


Figure 6.7.8: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 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 6.7.9. 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.

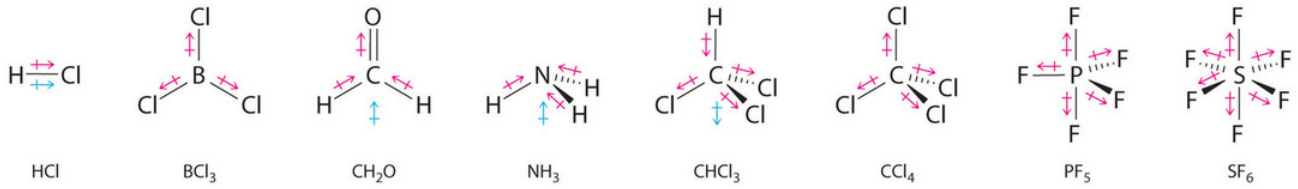
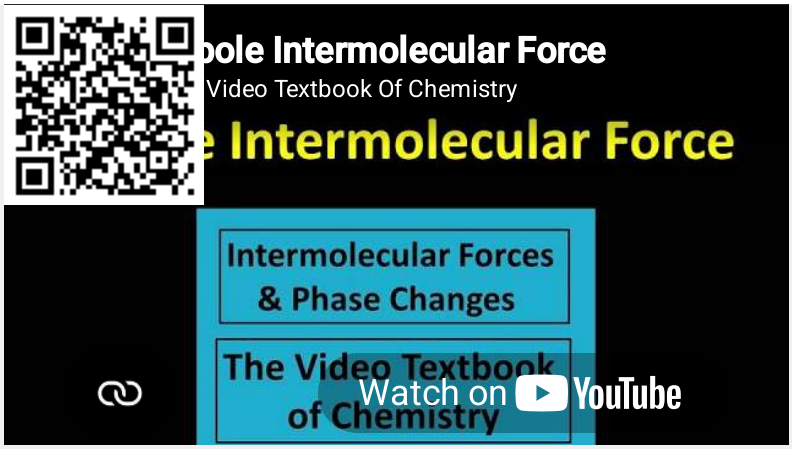


Figure 6.7.9: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).



Example 6.7.4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

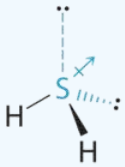
Asked for: net dipole moment

Strategy:

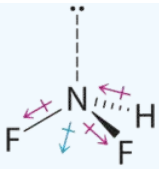
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

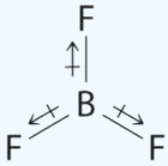
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 6.7.6). The bond dipoles cannot cancel one another, so the molecule has a net 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 6.7.4

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer

CH_3Cl and XeO_3

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.

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6.8: VSPER Theory- The Effect of Lone Pairs

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.

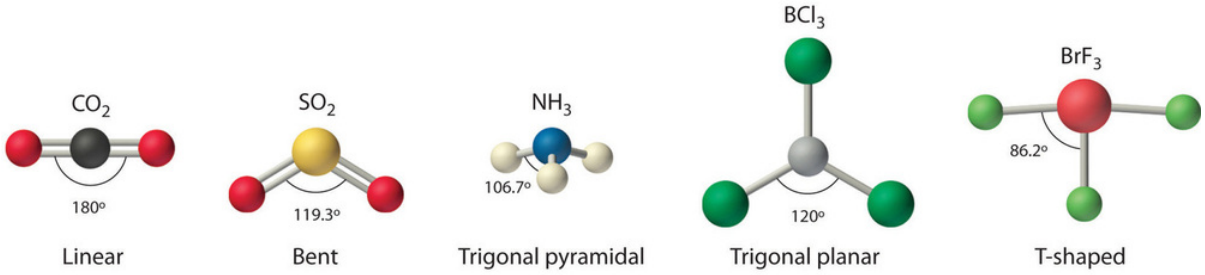


Figure 6.8.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

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 6.8.1 and 6.8.2.

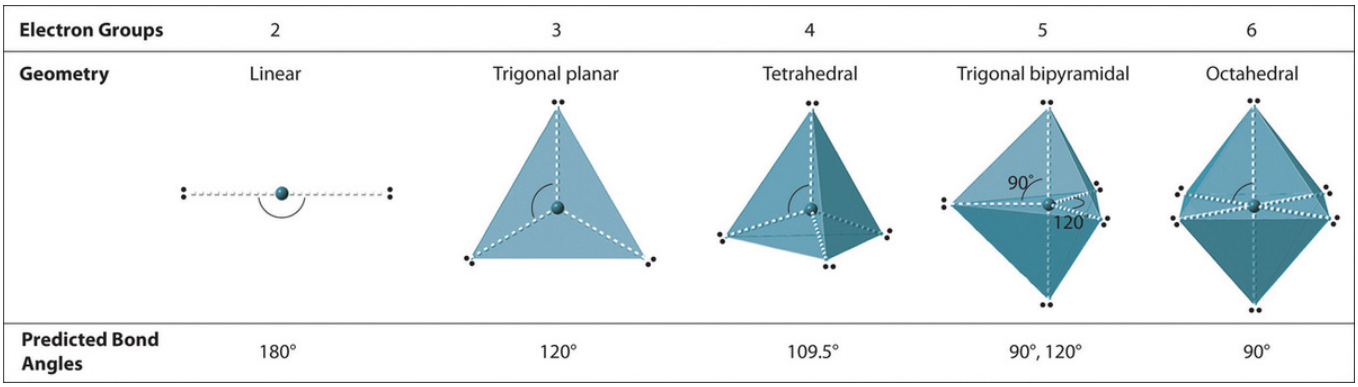


Figure 6.8.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

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 6.8.2 and Figure 6.8.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

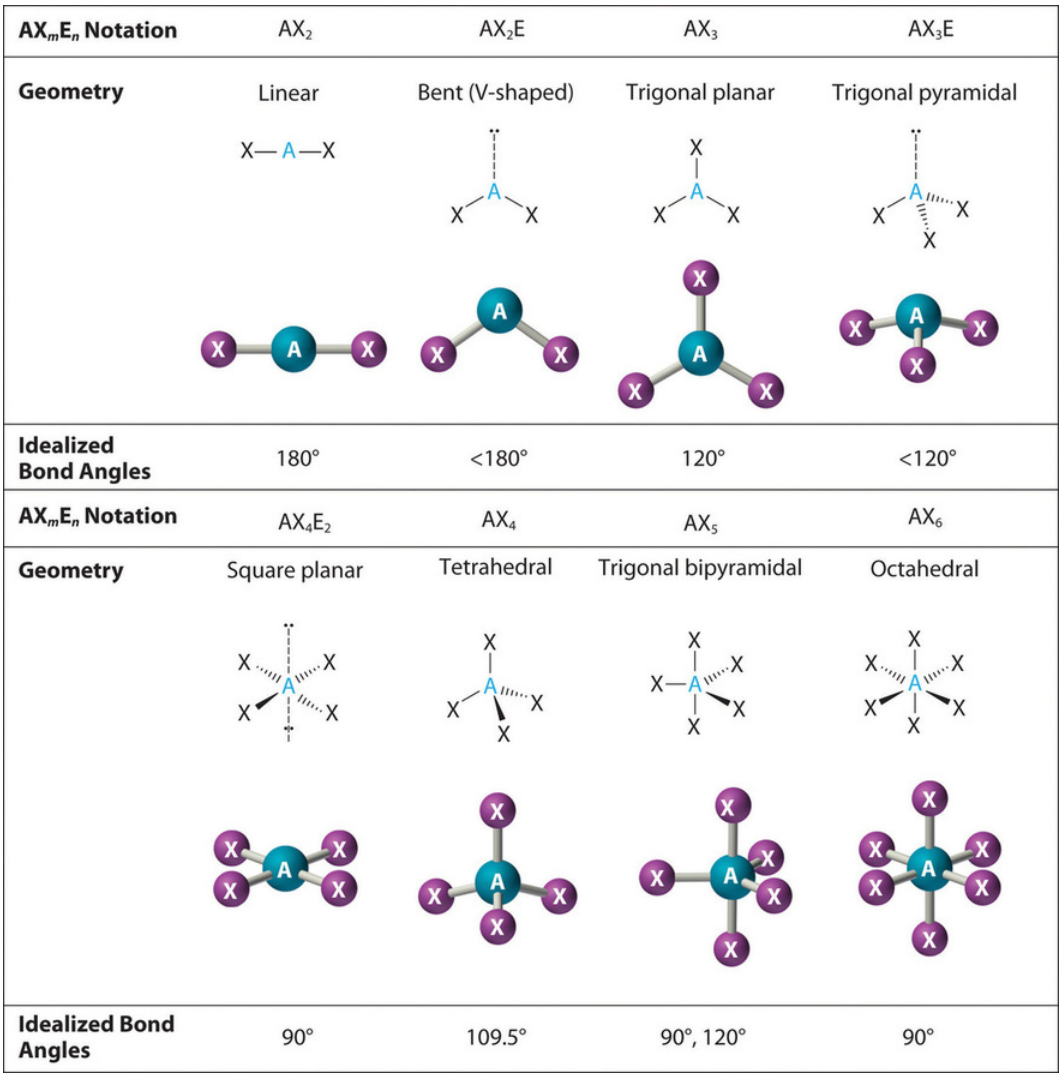


Figure 6.8.3: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

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

H:Be:H or H—Be—H

Lewis structure

Figure 6.8.2 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 6.8.3 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.

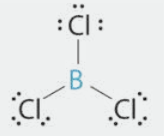
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

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 6.8.3). The structure of CO_2 is shown in Figure 6.8.1.

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

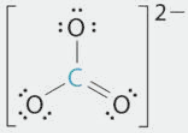
Figure 6.8.2): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 6.8.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 6.8.2.

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



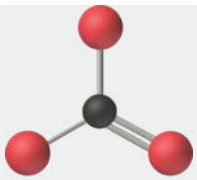
Lewis structure

Figure 6.8.2).

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 6.8.3 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.

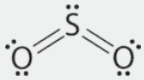


Figure 6.8.2): (CC BY-NC-SA; anonymous)

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 6.8.4). 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 6.8.2 and 6.8.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

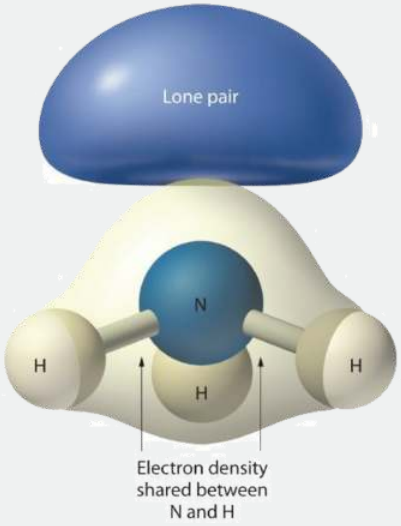
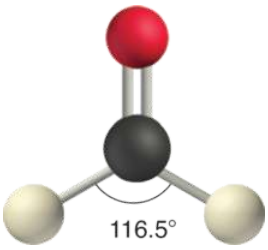


Figure 6.8.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

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°).

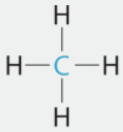


Four Electron Groups

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

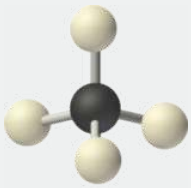


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 6.8.2, 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.

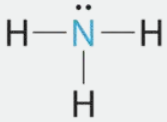
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 6.8.3).



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 6.8.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 6.8.3 and Figure 6.8.4).

AX_2E_2 Molecules: H_2O

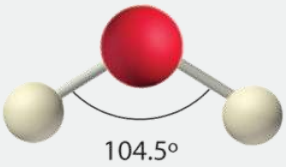
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



Figure 6.8.2: (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

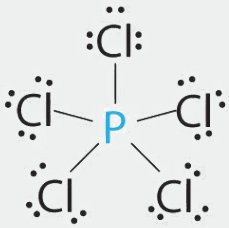
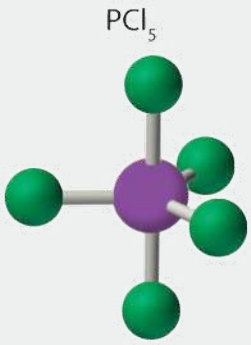


Figure 6.8.2): (CC BY-NC-SA; anonymous)

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 6.8.3. 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 6.8.2.

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.

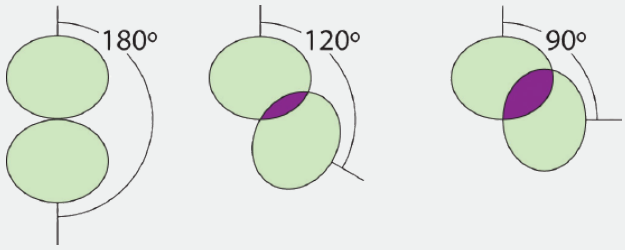
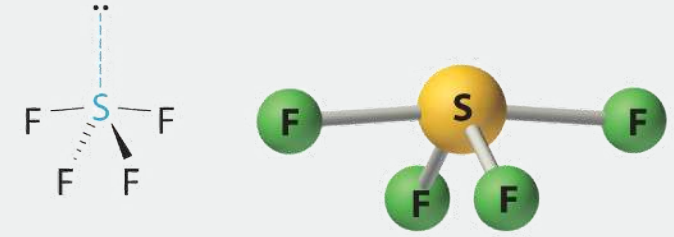


Figure 6.8.5: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

180 degree angle has no shared space between teo electron pair, 120 degree angle has some shared area between two electron pairs. 90 degree angle has more shared space than 120.

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

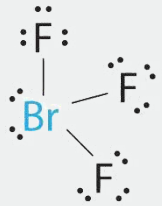
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2 Molecules: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Three fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has two lone pairs.

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

If the lone pairs are axiam, the 90 degree LP-LP interactions are o and the 90 degree LP-BP interaction is zero. If the Lone pares are equatorial there are zero 90 degree LP-LP interactions and four 90 degree LP-BP intereactions. If the lone pairs are axial and equatorial there is one 90 degree LP-LP interaction and three 90 degree LP-BP interaction.

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP

repulsions (Figure 6.8.2.1).

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.

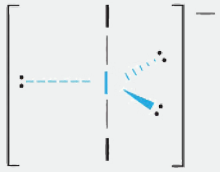
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



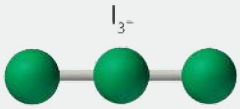
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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 6.8.2.)

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



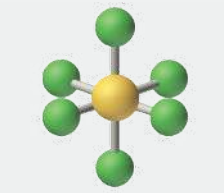
Lewis structure

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 6.8.2 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.

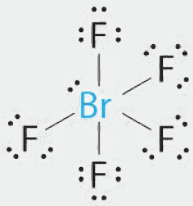
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



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

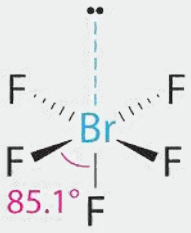


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

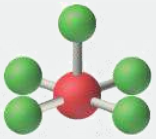
With its expanded valence, this species is an exception to the octet rule.

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.

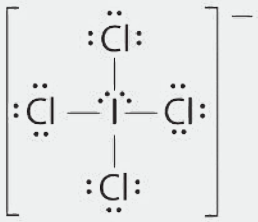
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



Molecular geometry
(square pyramidal)

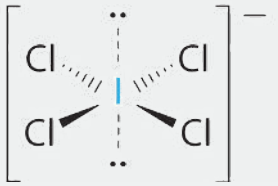
AX_4E_2 Molecules: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



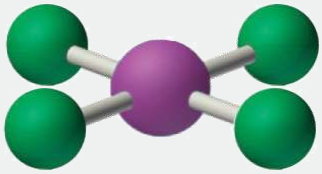
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

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 6.8.6.

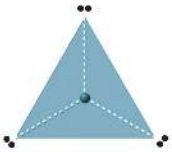
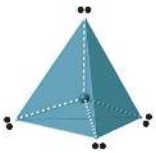
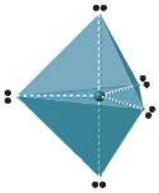
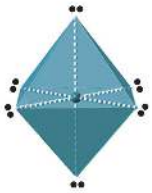
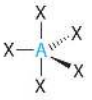
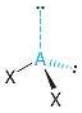
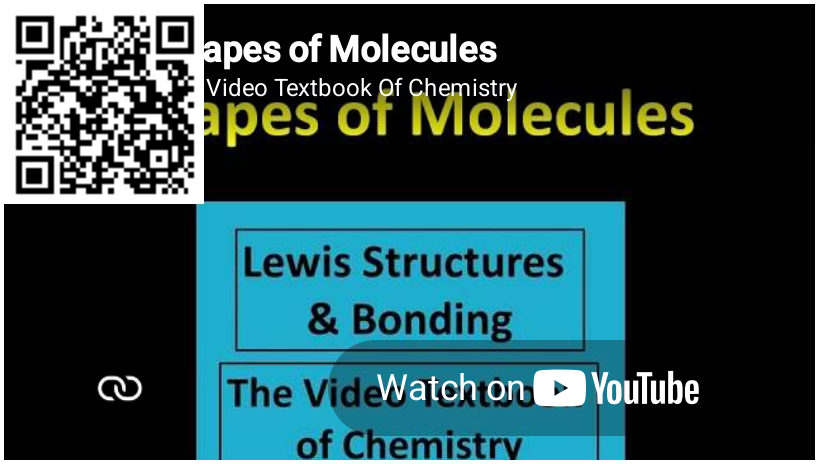
Electron Groups	2	3	4	5	6
Molecular Geometry					
	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Zero Lone Pairs					
	Linear AX_2	Trigonal planar AX_3	Tetrahedral AX_4	Trigonal bipyramidal AX_5	Octahedral AX_6
One Lone Pair					
		Bent (V-shaped) AX_2E	Trigonal pyramidal AX_3E	Seesaw AX_4E One axial lone pair	Square pyramidal AX_5E
Two Lone Pairs					
			Bent (V-shaped) AX_2E_2	T-shaped AX_3E_2 Two axial lone pairs	Square planar AX_4E_2
Three Lone Pairs					
				Linear AX_2E_3 Three axial lone pairs	

Figure 6.8.6***:*** *Overview of Molecular Geometries*



Example 6.8.1

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

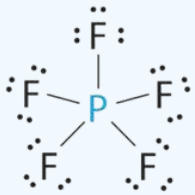


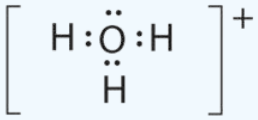
Figure 6.8.6): (CC BY-NC-SA; anonymous)

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

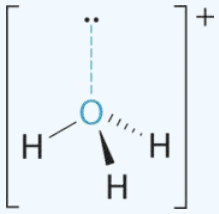


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

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 6.8.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

Example 6.8.2

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 Example6.8.1.

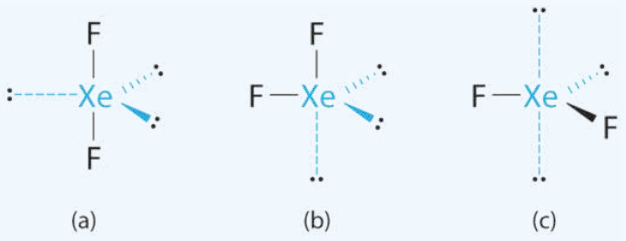
Solution:

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

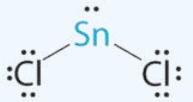
If the two F atoms are axial ther are zero 90 LP-LP interactions. If the two F atoms are axial and equatorial or just equatorial, there are 2 90 LP-LP interactions.

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 6.8.2

Predict the molecular geometry of each molecule.

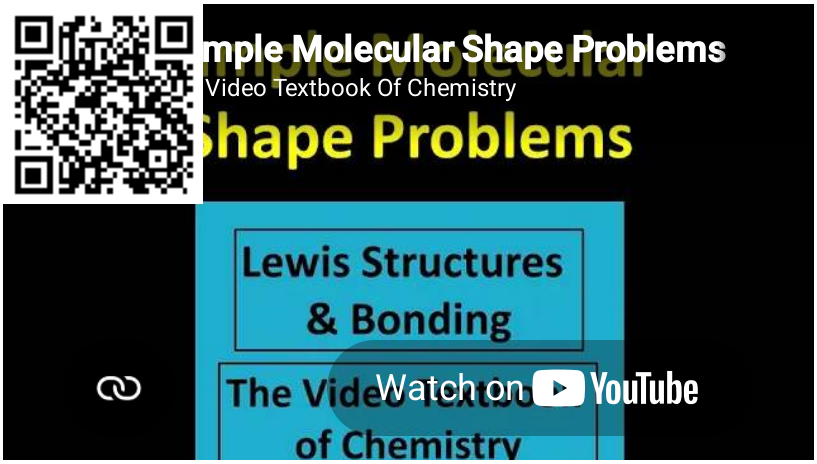
a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

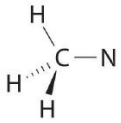


Molecules with No Single Central Atom

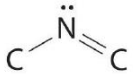
The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. 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:

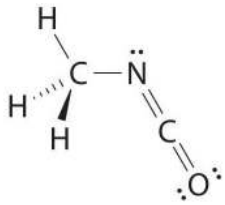


Figure 6.8.7).

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.

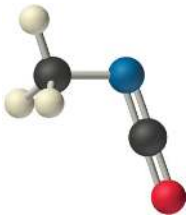


Figure 6.8.7: The Experimentally Determined Structure of Methyl Isocyanate

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 6.8.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), 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 6.8.3 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 6.8.3

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

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

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 6.8.8*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 6.8.8*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.

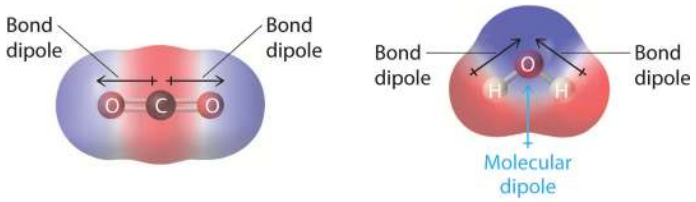


Figure 6.8.8: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 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 6.8.9. 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.

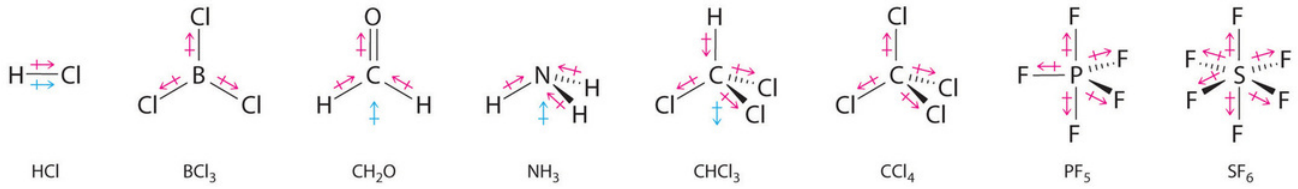
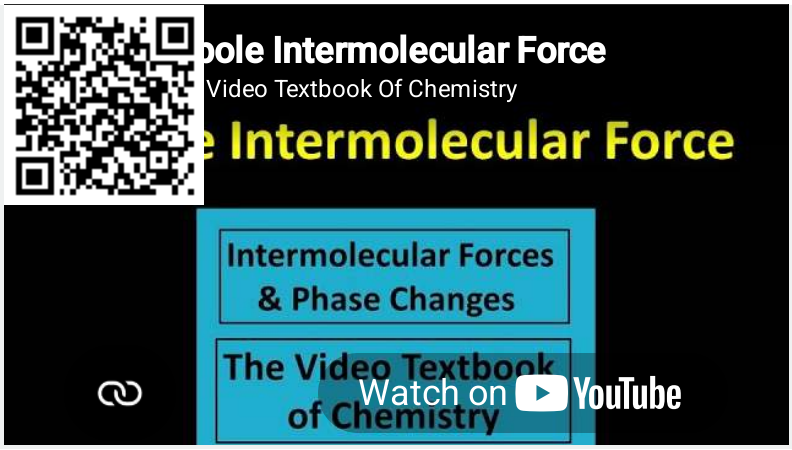


Figure 6.8.9: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).



Example 6.8.4

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

Given: three chemical compounds

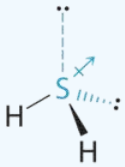
Asked for: net dipole moment

Strategy:

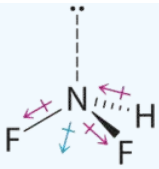
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

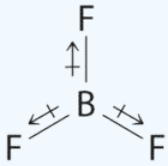
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 6.8.6). The bond dipoles cannot cancel one another, so the molecule has a net 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 6.8.4

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer

CH_3Cl and XeO_3

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.

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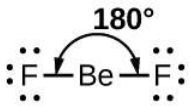
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6.9: VSPER Theory - Predicting Molecular Geometries

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 6.9.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 6.9.2).



A Lewis structure is shown. A fluorine atom with three lone pairs of electrons is single bonded to a beryllium atom which is single bonded to a fluorine atom with three lone pairs of electrons. The angle of the bonds between the two fluorine atoms and the beryllium atom is labeled, “180 degrees.”

Figure 6.9.2: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 6.9.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

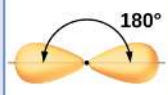
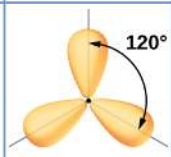
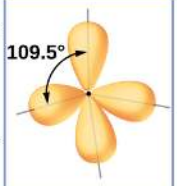
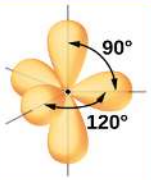
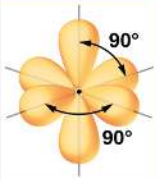
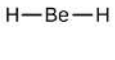
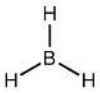
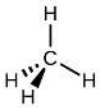
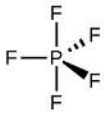
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 6.9.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

In this table summarizing the geometries proposed by VSPER Theory, the number of regions along with spatial arrangement, line-dash-wedge notation, and electron pair geometry are shown.

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6.10: Molecular Shape and Polarity

Learning Objectives

- To calculate the percent ionic character of a covalent polar bond

Previously, we described the two idealized extremes of chemical bonding:

- **ionic bonding**—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and
- **covalent bonding**, in which electrons are shared *equally* between two atoms.

Most compounds, however, have polar covalent bonds, which means that electrons are shared *unequally* between the bonded atoms. Figure 6.10.1 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a *polar bond*.

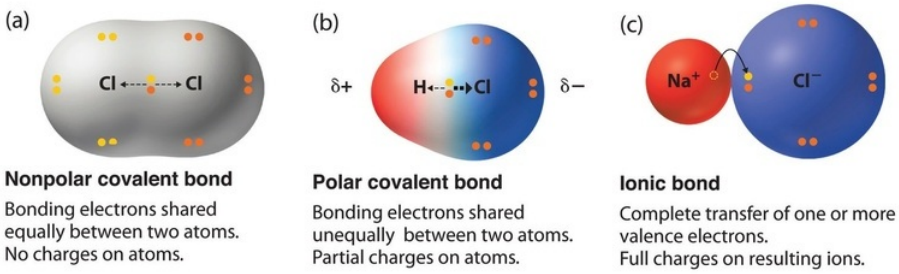


Figure 6.10.1: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. *Electronegativity* (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{less\ electronegative}{A}} - \underset{\delta^-}{\overset{more\ electronegative}{B}} \tag{6.10.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms:

$$\Delta\chi = \chi_B - \chi_A.$$

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms (Table A2): $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq\approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and

Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in $NaCl$, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a dipole moment where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \tag{6.10.2}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{6.10.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 6.10.2).

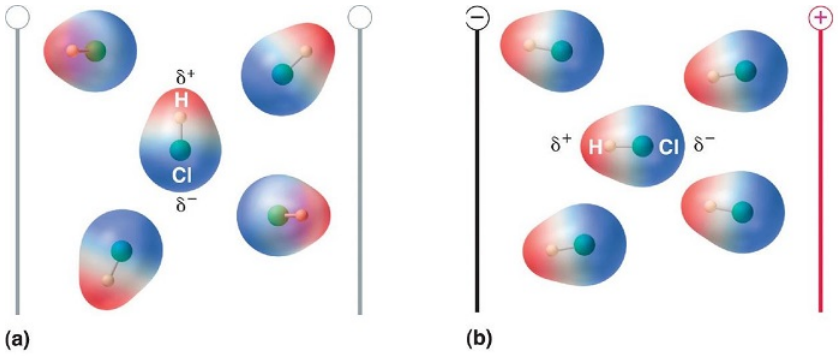


Figure 6.10.2: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), theHClmolecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 6.10.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) \\ &= 2.901 \times 10^{-20}\ C \end{aligned}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution inHCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20} \cancel{C}}{1.6022 \times 10^{-19} \cancel{C}} = 0.1811\ e^- \tag{6.10.4}$$

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

$$\overset{0.18\delta^+}{H} - \overset{0.18\delta^-}{Cl}$$

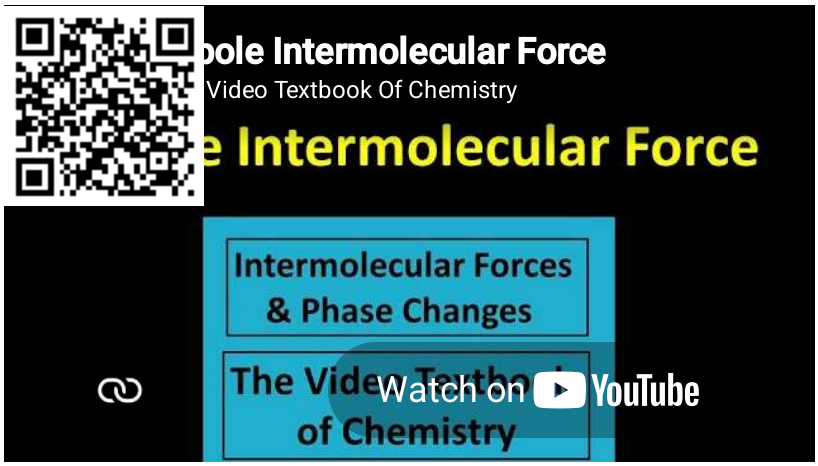
Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine ($\chi_H = 2.20$ and $\chi_{Cl} = 3.16$) so

$$\chi_{Cl} - \chi_H = 0.96$$

This is a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.



A warning about Dipole Moment arrows

As the figure above shows, we represent dipole moments by an arrow with a length proportional to μ and pointing from the positive charge to the negative charge. However, the **opposite** convention is still widely used especially among physicists.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 6.10.2 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as $NaCl_{(g)}$ and $CsF_{(g)}$ is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 6.10.2 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 6.10.1.

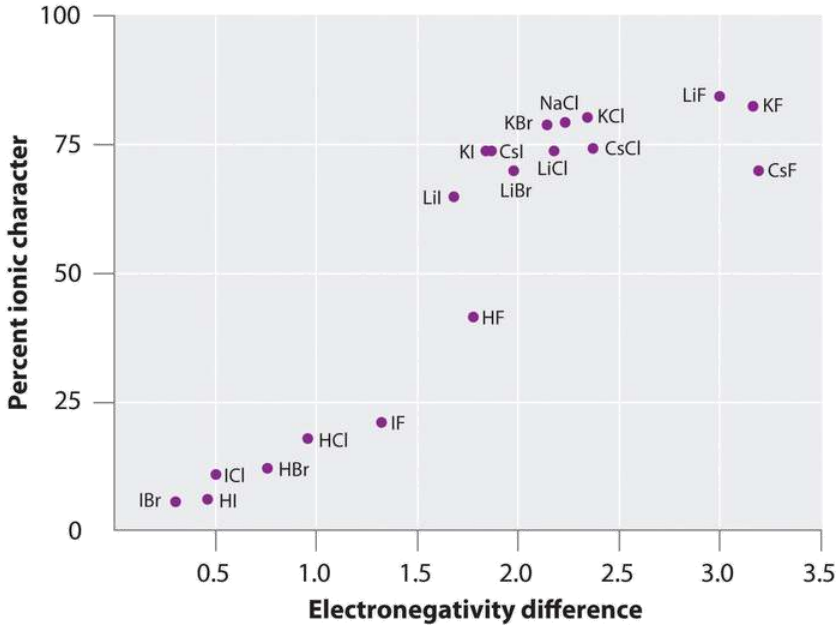


Figure 6.10.2: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms. In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 6.10.1: percent ionic character

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A. Compute the charge on each atom using the information given and Equation 6.10.2

B. Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) \\ &= 1.272 \times 10^{-19}\ C \end{aligned}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\begin{aligned} \text{ionic character} &= \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) \\ &= 79.39\% \simeq 79\% \end{aligned}$$

Exercise 6.10.1

In the gas phase, silver chloride ($AgCl$) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity.

$$\mu = Qr$$

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

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CHAPTER OVERVIEW

7: Chemical Bonding II- Valance Bond Theory, and Molecular Orbital Theory

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7.3: Valence Bond Theory- Hybridization of Atomic Orbitals

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7.1: Oxygen- A Magnetic Liquid



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7.2: Valence Bond Theory- Orbital Overlap as a Chemical Bond

Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

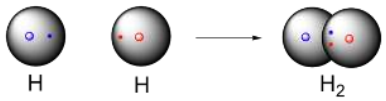
Introduction

As we have talked about using Lewis structures to depict the bonding in covalent compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in covalent molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

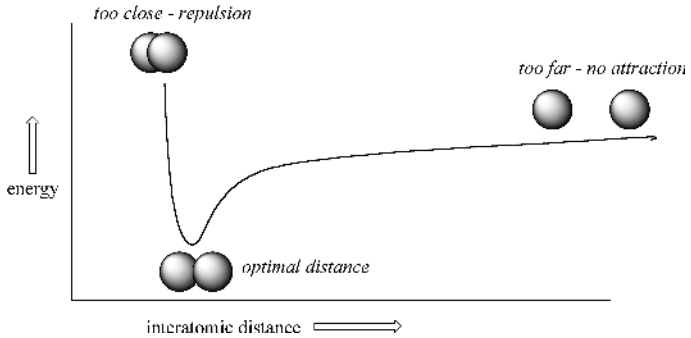
Example: The H_2 molecule

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.



Graph of increasing energy against increasting interatomic distance. If the two are too close there is repulsion, if the two are too far there is no attraction. There is an optimal distance.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74 x 10^{-12} meters, or 0.74 Å (Å means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about 1.5 Å long (Å means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about 1.3 Å, carbon-oxygen double bonds are about 1.2 Å, and carbon-hydrogen bonds are in the range of 1.0 – 1.1 Å. Most covalent bonds in organic molecules range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole. You can refer to tables in reference books such as the CRC Handbook of Chemistry and Physics for extensive lists of bond lengths, strengths, and many other data for specific organic compounds.

Balls and Springs

Although we tend to talk about "bond length" as a specific distance, it is not accurate to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important, when we study the analytical technique known as infrared (IR) spectroscopy.

Valence Bond Theory: A Localized Bonding Approach

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure 7.2.1). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* 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 7.2.1).

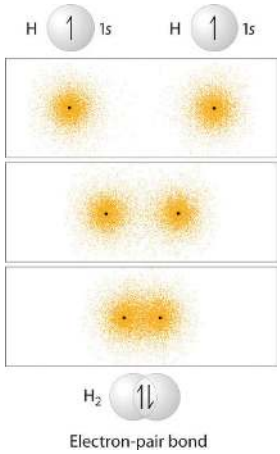


Figure 7.2.1: Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1*s* orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure 7.2.2 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 $n = 2$. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "pointing at" each other) and are *in phase* (represented by colors in Figure 7.2.2).

> Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

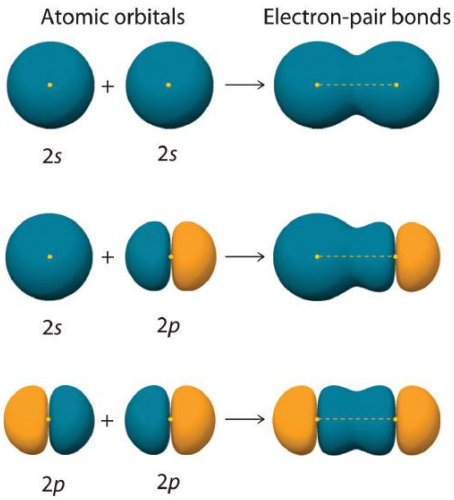
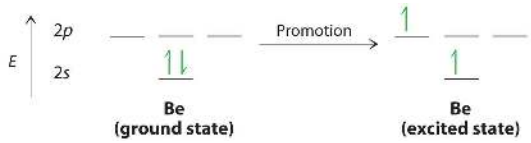


Figure 7.2.2 : Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

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 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the

maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:



The ground state of beryllium has one electron pair in the 2s orbital. The excited state of beryllium takes one of the electrons from the 2s orbital and moves it to the 2p orbital.

In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce $\mathrm{BeH_2}$, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* 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 $\mathrm{BeH_2}$ form, scientists developed the concept of hybridization.

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7.3: Valence Bond Theory- Hybridization of Atomic Orbitals

The localized **valence bond theory** uses a process called **hybridization**, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 7.3.1.

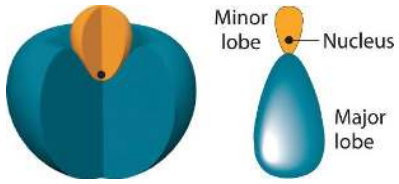


Figure 7.3.1**:** The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A − B can also be written as A + (−B), in Figure 7.3.2 and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by −1 and adding. This gives us Equation 7.3.2, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{7.3.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{7.3.2}$$

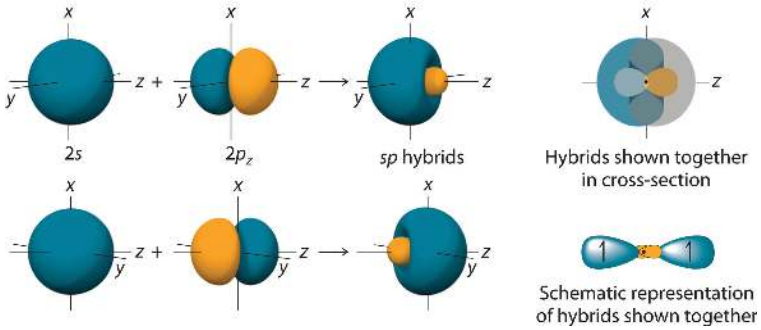


Figure 7.3.2: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:

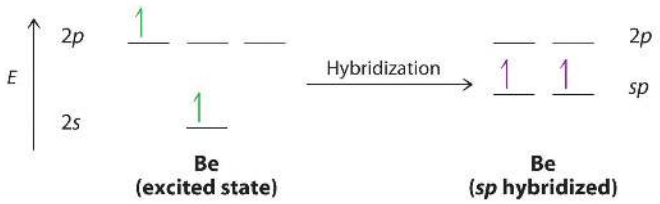


Figure 7.3.3. each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure 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.

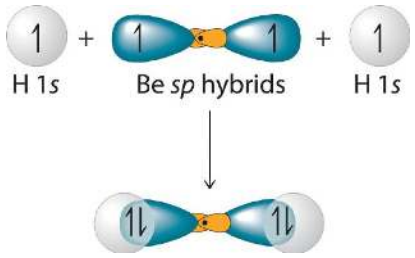


Figure 7.3.3: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule 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 7.3.4). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

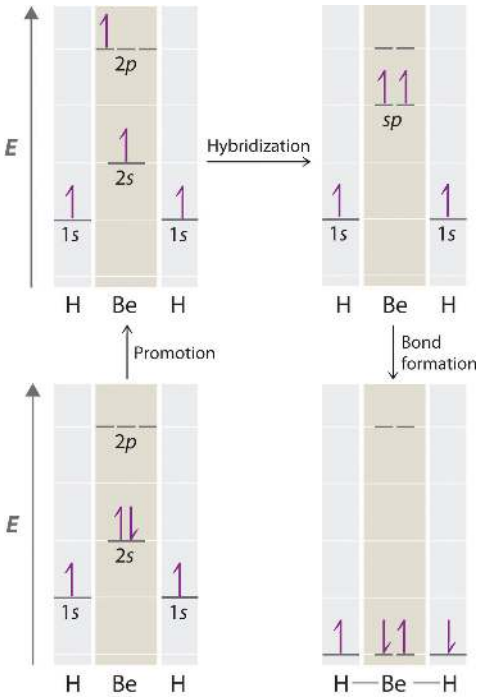
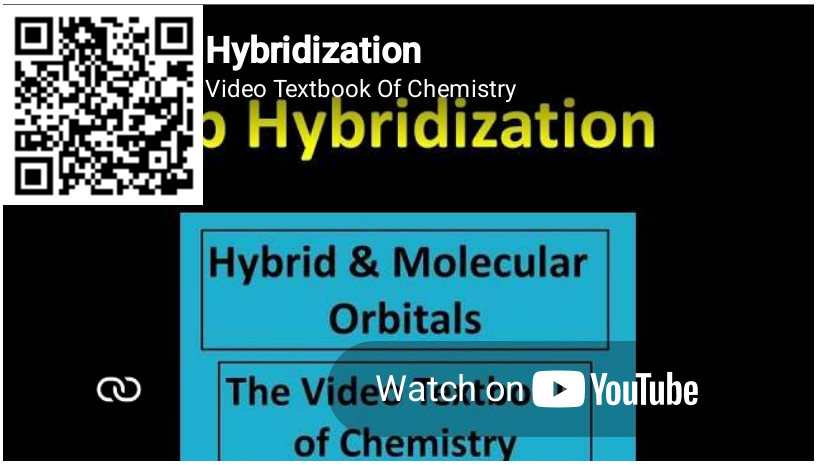


Figure 7.3.4: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable *only* if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.



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:

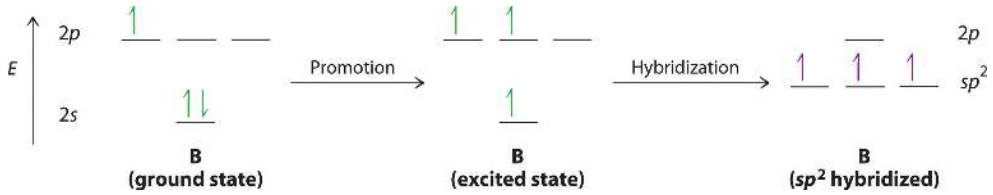


Figure 7.3.5). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

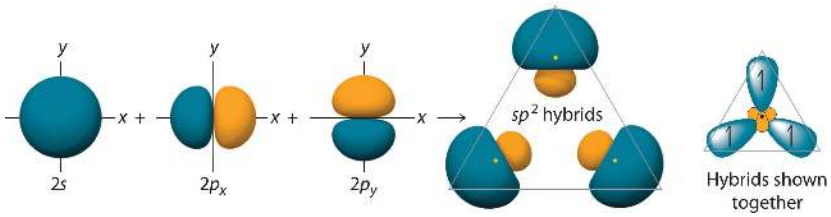
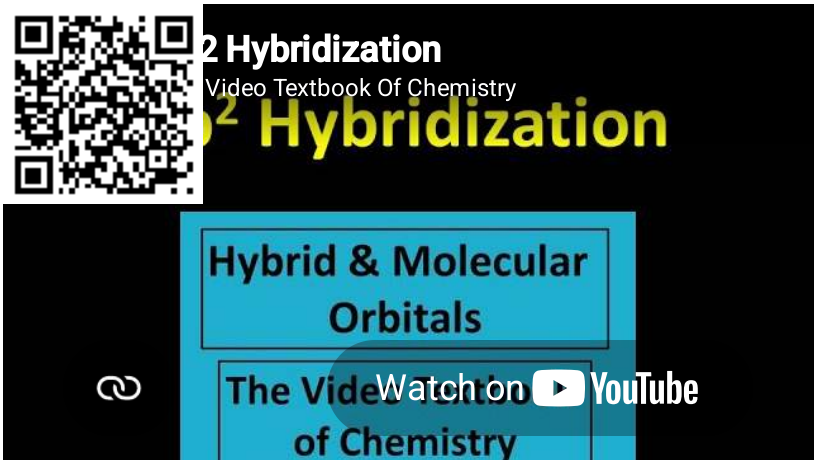


Figure 7.3.5: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.



Looking at the $2s^2 2p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent

bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:

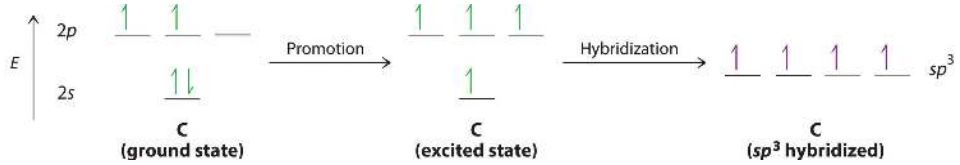


Figure 7.3.6). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

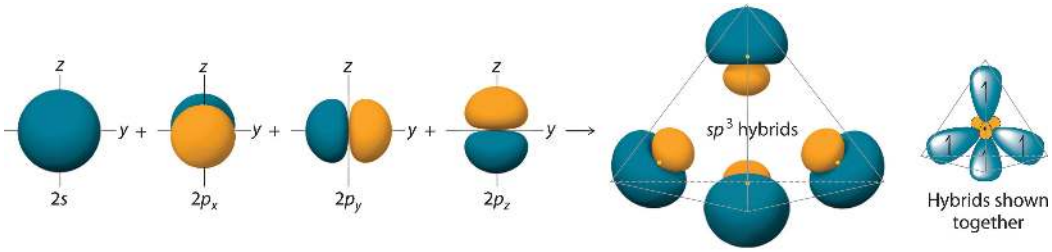
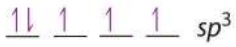


Figure 7.3.6: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

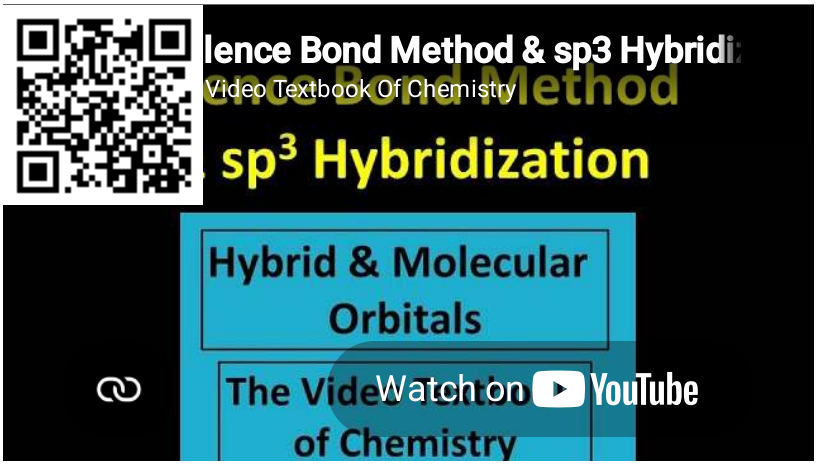
In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that only form in certain chemical reactions.

> *Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.*

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^2 2p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:



The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in NH_3 and H_2O, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.



Example 7.3.1

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 VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise 7.3.1

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.

Answer 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 7.3.7). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure 9.5.6). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

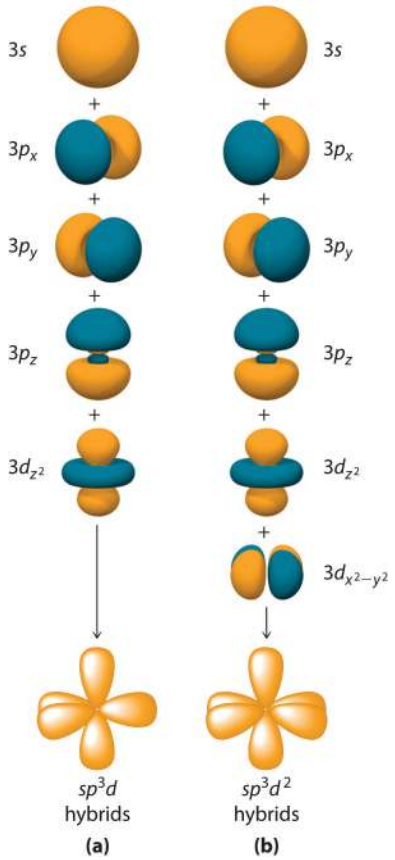


Figure 7.3.7: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 7.3.2

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

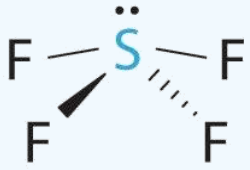
Asked for: hybridization of the central atom

Strategy:

A. Determine the geometry of the molecule using the strategy in Example 7.3.1. 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 7.3.2

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

Answer a

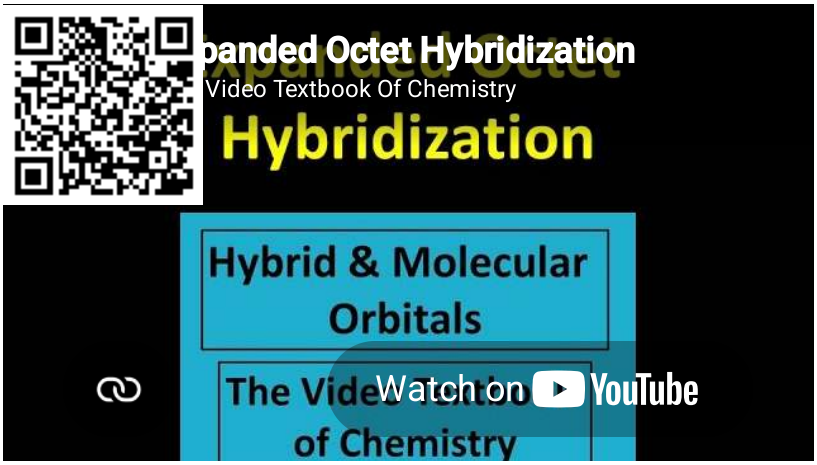
sp^3d with three Br–F bonds and two lone pairs

Answer a

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 2*s*, 2*p*, and 3*d* atomic orbitals. The 3*d* orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.



Example 7.3.3: 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 2*s* and 2*p* valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise 7.3.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer a

sp^3d^2 hybridization; no

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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7.4: Molecular Orbital Theory- Electron Delocalization

Learning Objectives

- To use molecular orbital theory to predict bond order

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Molecular Orbital Theory: A Delocalized Bonding Approach

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in Chapter 9, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) = &\quad AO(atom\ A) &+ &\quad AO(atom B) \\ MO(1) = &\quad AO(atom\ A) &- &\quad AO(atom B) \end{aligned} \tag{7.4.1}$$

The molecular orbitals created from Equation 7.4.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

> *A molecule must have as many molecular orbitals as there are atomic orbitals.*

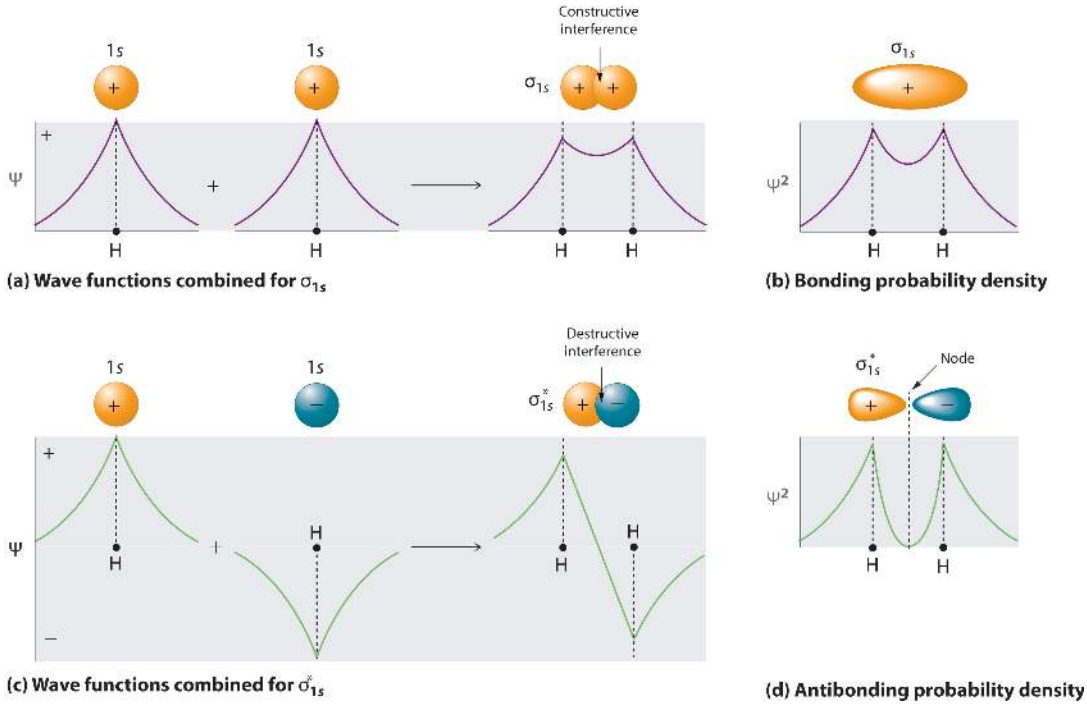


Figure 7.4.1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1*s* atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital 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 1*s* atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 7.4.1). In a sigma (σ) orbital, (i.e., a bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry), the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{7.4.2}$$

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 7.4.1). 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:

$$\sigma^\star_{1s} \approx 1s\,(A) - 1s\,(B) \tag{7.4.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma^\star_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^\star_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* 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 1*s* atomic orbitals. Consequently, the $\sigma^{\star}_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* 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 7.4.2

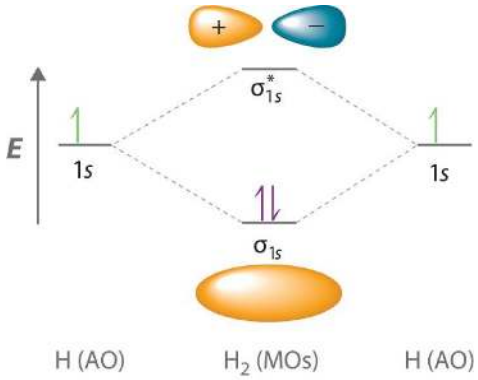


Figure 7.4.2: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more 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 7.4.2). 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:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{7.4.4}$$

To calculate the bond order of H_2, we see from Figure 7.4.2 that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2}=1 \tag{7.4.5}$$

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 7.4.2 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.

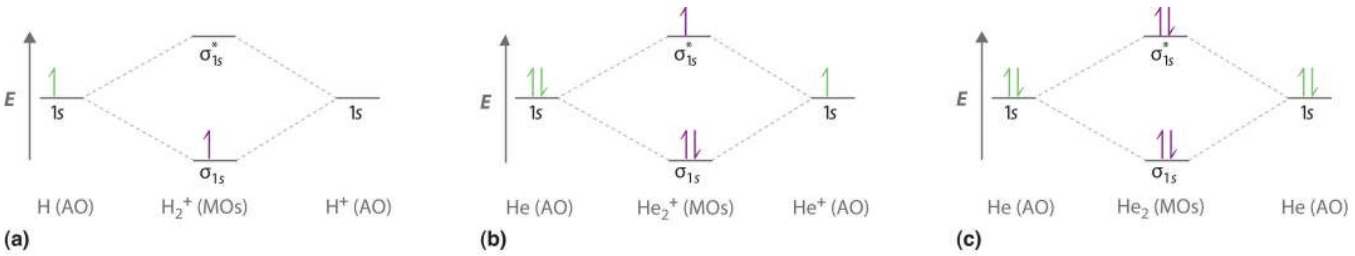


Figure 7.4.3: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

for the H2+ ion the H has one unpaired electron in the 1s orbital so the H2+ has one unpaired electron in the sigmas 1 s orbital. for He2+ ion, He has a full 1 s orbital and He+ has one upaired electron in the 1 s orbital. This means that the sigmal 1s orbital is full and the sigmal*1s orbital has one upaired electron. For the He2 molecule, each He has a full 1 s orbital. This means that sigma 1s and sigma * 1s orbital are full.

Figure 7.4.3*a* shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is

$$\frac{1-0}{2}=1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 7.4.1, these predictions agree with the experimental data.

Figure 7.4.3*b* is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma^\star_{1s}$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^\star_{1s})^1$ electron configuration. This electron configuration gives a bond order of

$$\frac{2-1}{2}=1/2$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 7.4.1).

Table 7.4.1: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

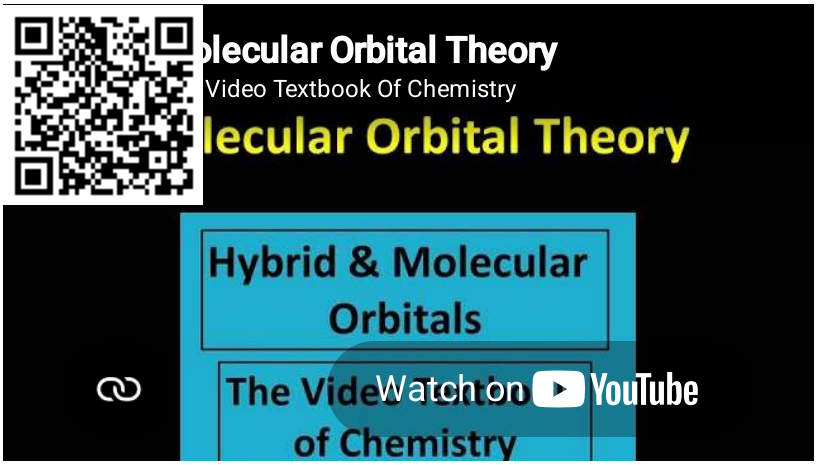
Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^\star_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^\star_{1s})^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure 7.4.3*c* 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 $(\sigma_{1s})^2 (\sigma^\star_{1s})^2$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

> *In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.*



Example 7.4.1

Use a molecular orbital energy-level diagram, such as those in Figure 7.4.2, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbital

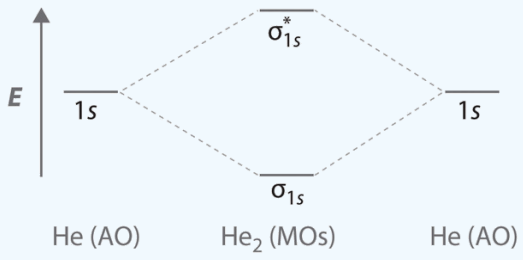
B. s. Draw the molecular orbital energy-level diagram for the system.

C. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

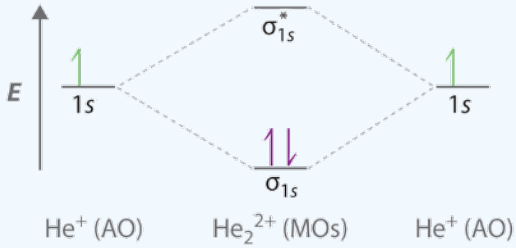
D. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma^\star_{1s}$ 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 1*s* atomic orbital. We can now fill the molecular orbital diagram:



Each He+ has one unpaired electron in the 1 s orbital. This means that He2 2+ has a full sigma 1 s orbital.

The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

? Exercise 7.4.1

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

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

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 7.4.4, 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 7.4.4. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

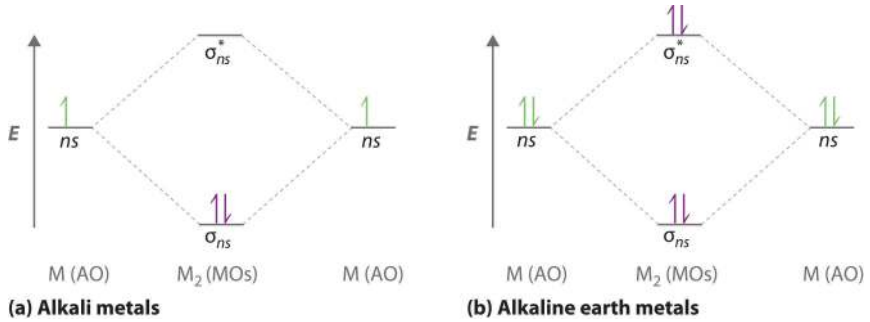


Figure 7.4.4 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic 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 7.4.2. As shown in part (b) in Figure 7.4.4, 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 7.4.2

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:

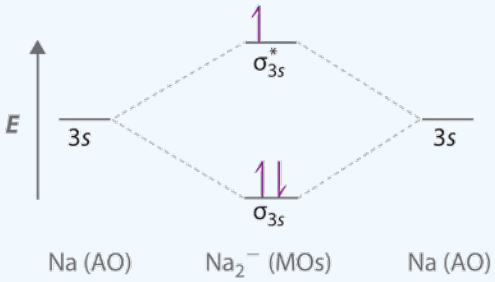
A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

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 1*s* atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2 (\sigma^*_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

? Exercise 7.4.2

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

Ca_2^+ has a $(\sigma_{4s})^2 (\sigma_{4s}^\star)^1$ electron configurations and a bond order of 1/2 and should exist.

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.

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{7.4.6}$$

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 7.4.5, 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):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{7.4.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{7.4.8}$$

In this combination, shown in part (b) in Figure 7.4.5, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

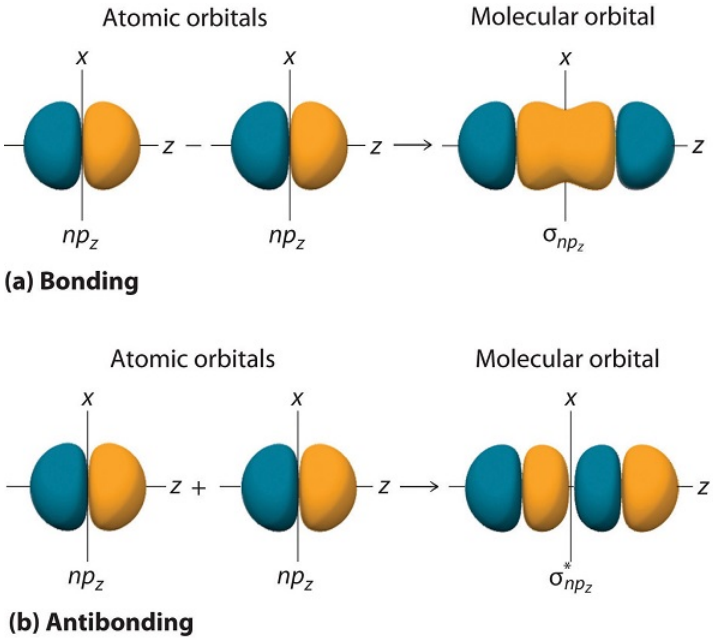


Figure 7.4.5 Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, 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 7.4.6, 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..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{7.4.9}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{7.4.10}$$

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.

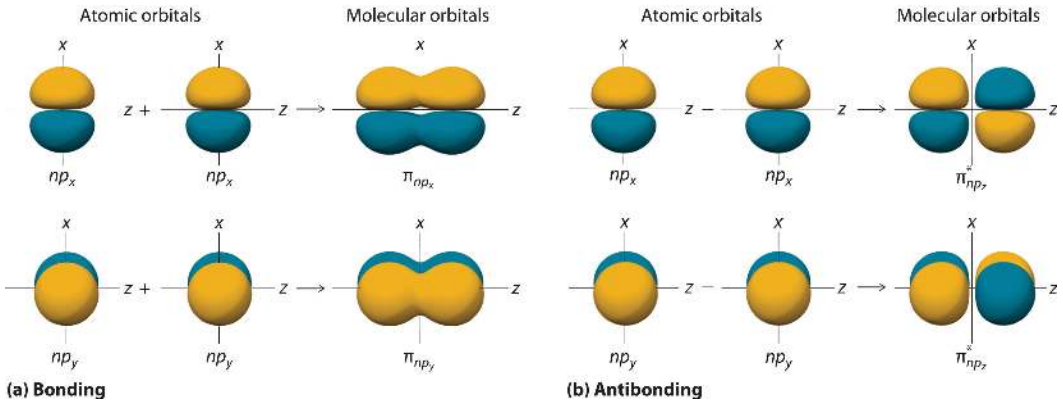


Figure 7.4.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) 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 7.4.7 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.

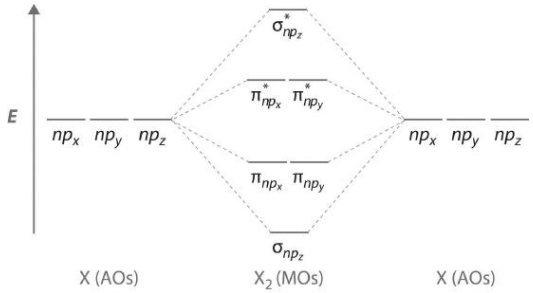


Figure 7.4.7 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals 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 7.4.8, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

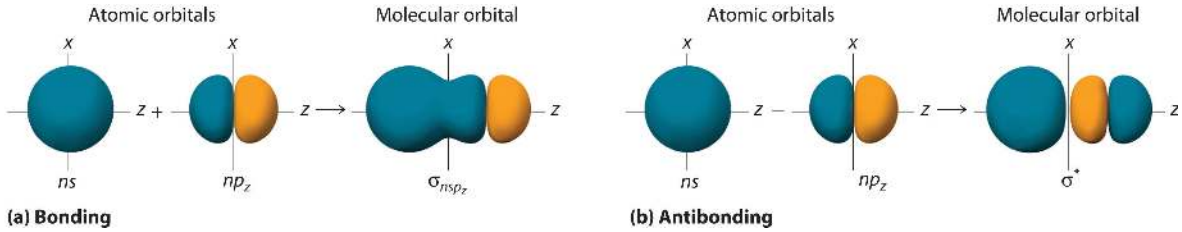


Figure 7.4.8 : Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Summary

Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach. A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

Learning Objectives

- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character. We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2.

four key points to remember when drawing molecular orbital diagrams:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the *"law of conservation of orbitals"*).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 7.4.1; the $n = 1$ orbitals (σ_{1s} and σ_{1s}*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

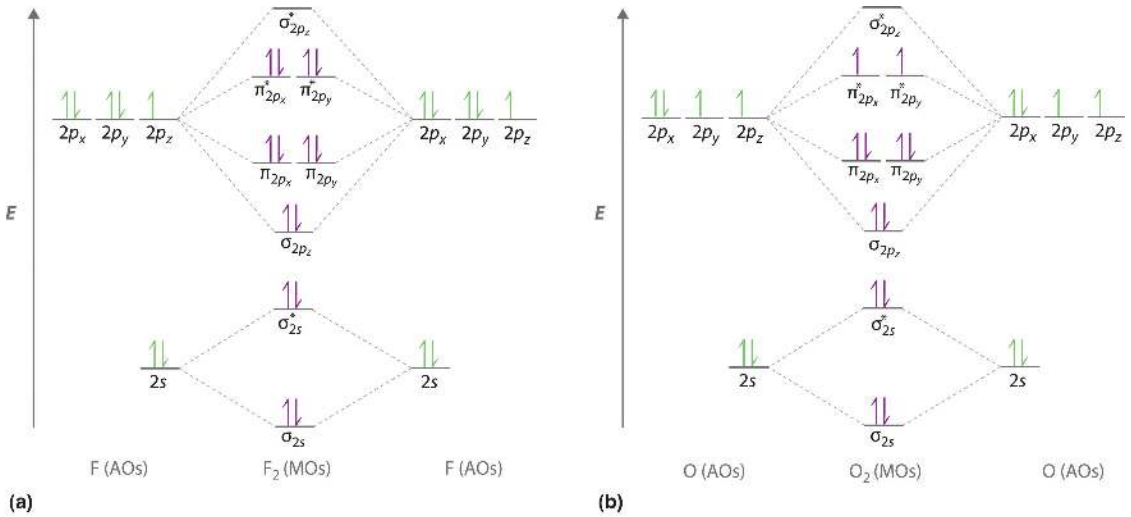


Figure 7.4.1: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^{\star}_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding 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 $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ 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 7.4.1. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π* orbitals

with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of (8 − 4) ÷ 2 = 2, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 7.4.2, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.

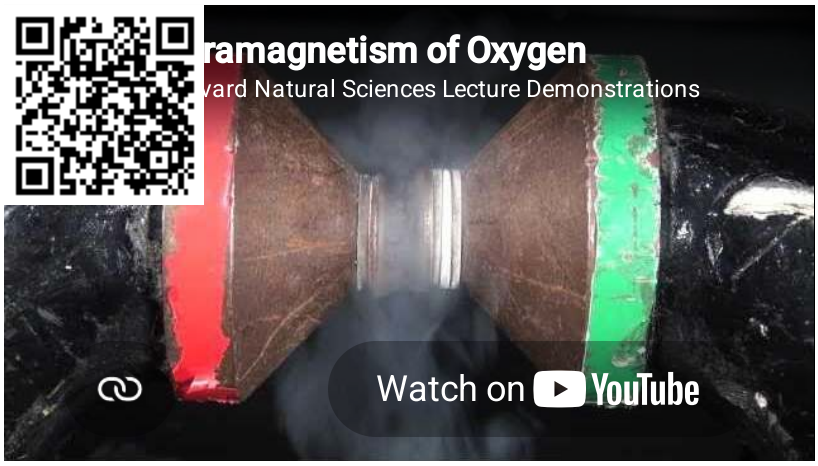


Figure 7.4.2: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ 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 7.4.3 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 7.4.3). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

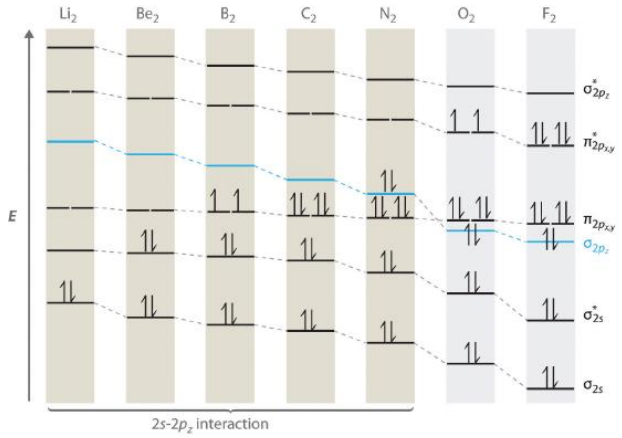


Figure 7.4.3: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

Example 7.4.3: Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

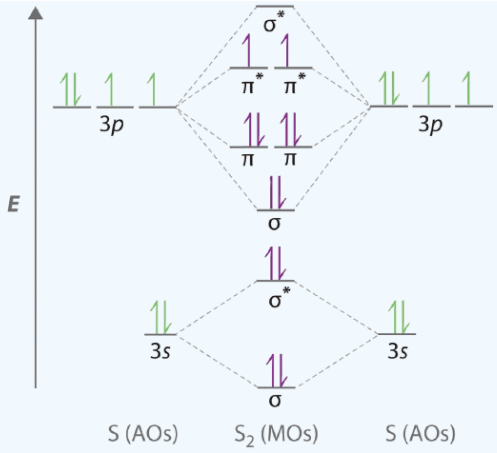
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 7.4.1 and Figure 7.4.3, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 7.4.3), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Two filled sigma orbitals, one filled sigma * orbital, two filled pi orbitals, and two pi * orbitals with one unpaired electron.

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ 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 $(\sigma_{3s})^2 (\sigma^{\star}_{3s})^2 (\sigma_{3p_z})^2 (\pi_{3p_{x,y}})^4 (\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? Exercise 7.4.3: The Peroxide Ion

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2 (\sigma^{\star}_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_{x,y}})^4 (\pi_{2p^{\star}_{x,y}})^4$ bond order of 1; no unpaired electrons

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 7.4.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

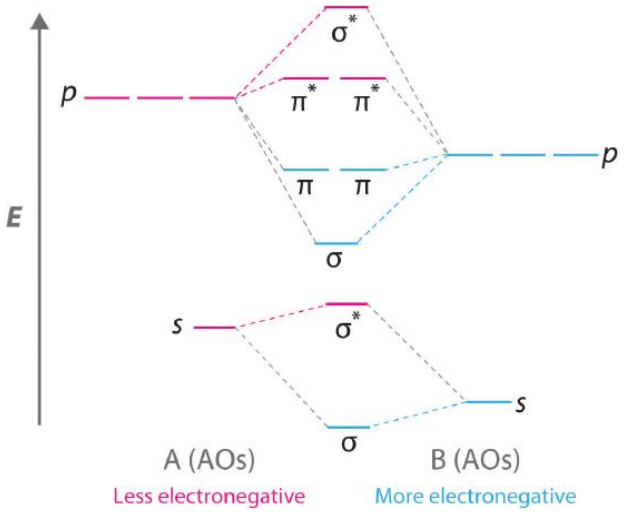


Figure 7.4.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 7.4.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 7.4.11). 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.

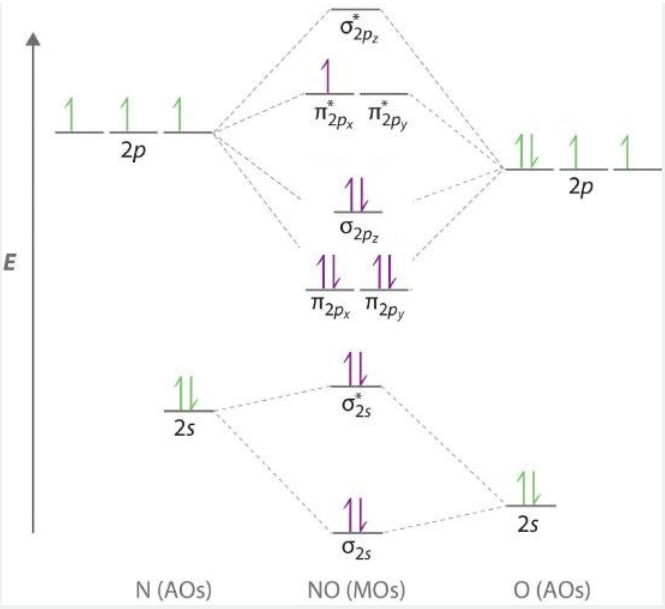


Figure 7.4.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_x},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\,(\sigma^{\star}_{2s})^2\,\left(\pi_{2p_{x,y}}\right)^4\,(\sigma_{2p_z})^2\,\left(\pi^{\star}_{2p_{x,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 7.4.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 7.4.13, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 7.4.6 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, 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 1*s* 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 $H^{\delta+}--Cl^{\delta-}$.

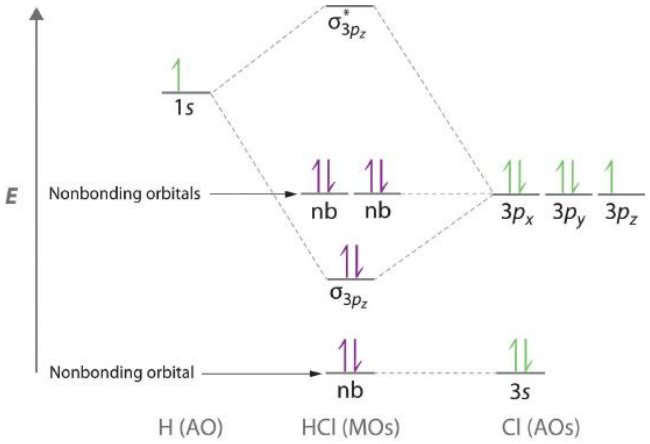


Figure 7.4.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have no effect on bond order.*

Example 7.4.4: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 7.4.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

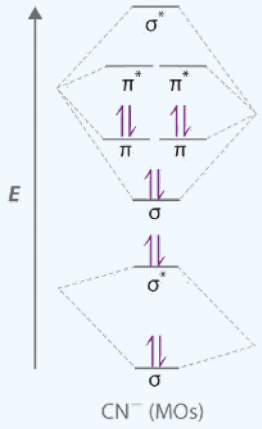
Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 7.4.4 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 7.4.4 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

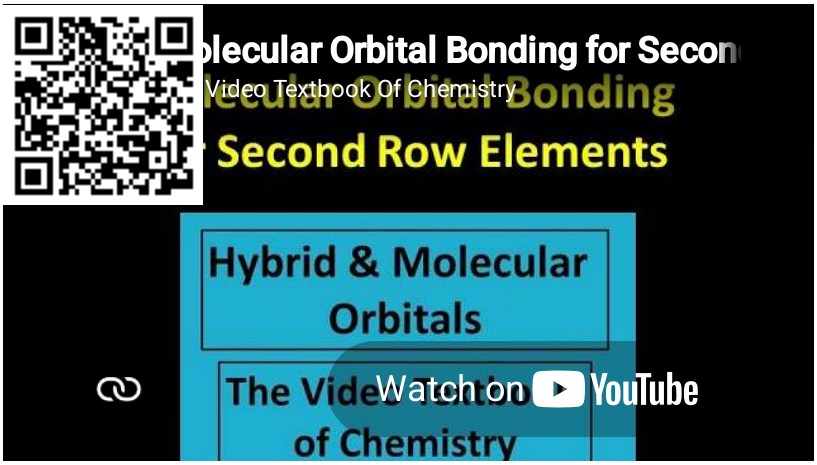
Exercise 7.4.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

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 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.

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CHAPTER OVERVIEW

8: Chemical Reactions and Chemical Quantities

8.1: Climate Change and the Combustion of Fossil Fuels

8.2: Chemical Change

8.3: Writing and Balancing Chemical Equations

8.4: Reaction Stoichiometry - How Much Carbon Dioxide?

8.5: Limiting Reactant, Theoretical Yield, and Percent Yield

8.6: Three Examples of Chemical Reactions- Combustion, Alkali Metals, and Halogens

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8.1: Climate Change and the Combustion of Fossil Fuels

Learning Objectives

- To use thermochemical concepts to discuss 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 fossil fuel energy and their impact on the environment.

Driven by environmental concerns about climate change and pollution, the world is undergoing a transformation from fossil fuels to renewable resources such as solar, and wind. The role that hydro and nuclear energy will play is uncertain and especially in the later case a policy rather than a scientific issue.

Fossil 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.

Fossil fuels, coal, oil and natural gas are the result of anaerobic decay of dead plants and animals laid down hundreds of millions of years ago, most of which took place well before the dinosaurs strode the earth. Fossil fuels slowly formed as further geological layers compressed and heated the dead organic matter. The energy content of fossil fuels results from the transformation of sunlight into vegetation and the chemical transformation brought about by anaerobic cooking at high pressures and temperatures over geological times.

Figure 15.7.1 represents a plant for generating electricity using oil or coal where the fuel is burned in a boiler, superheating steam which then powers a turbine for electrical generation. Oil derived fuels are seldom used in large power plants but diesel is used commonly in small electrical generators either in remote locations or as back up for when electrical distribution systems fail. Natural gas fueled power plants burn the fuel directly in the turbine which is similar to a jet engine. Coal power plants can convert ~40% of the energy released from combustion to electricity. In comparison, nuclear power plants can be more than 50% efficient and gas turbines can approach 60% mostly due to higher operating temperatures. Co-generation, using the plant to produce not only electricity but also heat for industrial or other purposes can raise overall efficiency by 10 - 15 % or so.

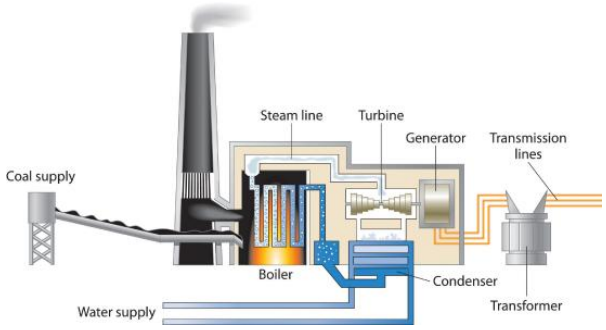


Figure 15.7.1 Electricity from Coal *A coal-powered electric power plant uses the combustion of coal to produce steam, which drives a turbine to produce electricity.*

The total expenditure of energy in the world each year is about 3×10^{21} kJ. Today, more than 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 2009 are shown in Figure 15.7.2.) but as Table 15.7.1 from the Wikipedia shows, energy usage is a complex issue. Petroleum dominates as a source of energy for transportation because gasoline is easy to transport, but is very little used for electrical generation, whereas 91% of coal is used for electrical generation. The other major use of coal is as a reducing agent for metal refining from ores. The former is called thermal coal, the latter metallurgical coal.

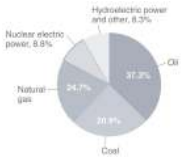
Table 15.7.1: Energy useage in the United States for 2008

Supply Sources	Percent of Source	Demand Sectors	Percent of Sector
Petroleum 37.1%	71% Transportation 23% Industrial 5% Residential and Commercial 1% Electric Power	Transportation 27.8%	95% Petroleum 2% Natural Gas 3% Renewable Energy
Natural Gas 23.8%	3% Transportation 34% Industrial 34% Residential and Commercial 29% Electric Power	Industrial 20.6%	42% Petroleum 40% Natural Gas 9% Coal 10% Renewable Energy
Coal 22.5%	8% Industrial <1% Residential and Commercial 91% Electric Power	Residential and Commercial 10.8%	16% Petroleum 76% Natural Gas 1% Coal 1% Renewable Energy
Renewable Energy 7.3%	11% Transportation 28% Industrial 10% Residential and Commercial 51% Electric Power	Electric Power 40.1%	1% Petroleum 17% Natural Gas 51% Coal 9% Renewable Energy 21% Nuclear Electric Power
Nuclear Electric Power 8.5%	100% Electric Power		

Coal

Coal was primarily laid down from the large swamp forests of the Carboniferous Period. Coal deposits are found today where those forests were 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 15.7.3). 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 15.7.2 Energy Consumption in the United States by Source, 2009



More than 80% of the total energy expended is provided by the combustion of fossil fuels, such as oil, coal, and natural gas.

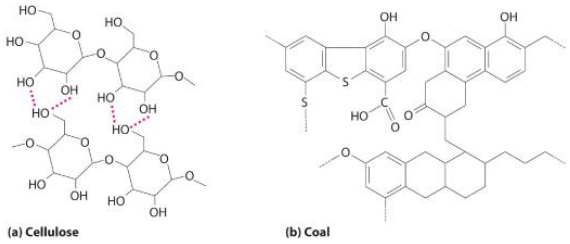


Figure 15.7.3 The Structures of Cellulose and Coal *(a) Cellulose consists of long chains of cyclic glucose molecules linked by hydrogen bonds. (b) When cellulose is subjected to high pressures and temperatures for long periods of time, water is eliminated, and bonds are formed between the rings, eventually producing coal. This drawing shows some of the common structural features of coal; note the presence of many different kinds of ring structures.*

There are four distinct classes of coal (Table 15.7.2); 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}. Lignite is extensively mined in Germany and Poland. 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. Anthracite is the first choice for metallurgical refining. The most abundant form in the Western United States in anthracite while that in the Eastern United States is bituminous coal, which has a high sulfur content because of the presence of small particles of pyrite (FeS_2). Combustion of coal releases the sulfur in FeS_2 as SO_2, which is a major contributor to acid rain. Table 15.7.3 compares the ΔH_{comb} per gram of oil, natural gas, and coal with those of selected organic compounds.

Table 15.7.2 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

Table 15.7.3 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
CH_4 (methane)	−55.5
gasoline	−84
hydrogen	−143

Peat, a precursor to coal, is the partially decayed remains of plants that grow in the swampy areas of the Carboniferous Period. 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 15.7.4). If a peat bog were buried under many layers of sediment for a few million years, the peat would 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.

Converting Coal to Gaseous and Liquid Fuels



Figure 15.7.4 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.*

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. Methods to convert coal to gaseous fuels (*coal gasification*) or liquid fuels (*coal liquefaction*) exist, but are not particularly economical unless the prices of oil and natural gas are high. With the development of fracking and the subsequent fall in oil and natural gas prices interest in these processes has fallen however they have played an important role in the past. In the most common approach to coal gasification, coal reacts with steam to produce a mixture of CO and H_2 known as *synthesis gas*, or *syngas*:Because coal is 70%–90% carbon by mass, it is approximated as C in Equation 15.7.1

$$C\,(s) + H_2O\,(g) \rightarrow CO\,(g) + H_2\,(g) \quad \Delta H = 131\ kJ$$

Converting coal to syngas removes any sulfur present and produces a clean-burning mixture of gases. Syngas or town gas was used for cooking until the 1960s when natural gas pipelines were built. Because syngas contains carbon monoxide (CO) it is poisonous, which accounts for scenes in old movies where people were killed by sticking their heads into an oven and allowing the gas to flow.

Syngas is can 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:

$$\begin{array}{ll}
2C\,(s) + 2H_2O\,(g) \rightarrow \cancel{2CO\,(g)} + \cancel{2H_2\,(g)} & \Delta H_1 = 262\ kJ \\
\cancel{CO\,(g)} + \cancel{H_2O\,(g)} \rightarrow CO_2\,(g) + \cancel{H_2\,(g)} & \Delta H_2 = -41\ kJ \\
\cancel{CO\,(g)} + \cancel{3H_2\,(g)} \rightarrow CH_4\,(g) + \cancel{H_2O\,(g)} & \Delta H_3 = -206\ kJ \\
\hline
2C\,(s) + 2H_2O\,(g) \rightarrow CH_4\,(g) + CO_2\,(g) & \Delta H_3 = 15\ kJ
\end{array}$$

Techniques available for converting coal to liquid fuels are not 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.

Petroleum

The petroleum that is pumped out of the ground is a complex mixture of several thousand organic compounds including straight-chain alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons with four to several hundred carbon atoms. The identities and relative abundances of the components vary depending on the source. So Texas crude oil is somewhat different from Saudi Arabian crude oil. In fact, the analysis of petroleum from different deposits can produce a "fingerprint" of each, which is useful in tracking down the sources of spilled crude oil. For example, Texas crude oil is "sweet," meaning that it contains a small amount of sulfur-containing molecules, whereas Saudi Arabian crude oil is "sour," meaning that it contains a relatively large amount of sulfur-containing molecules.

Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Recall that distillation separates compounds on the basis of their relative volatility, which is usually inversely proportional to their boiling points. Part (a) in Figure 15.7.5 shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil. The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the feedstock, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) in Figure 15.7.5 shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

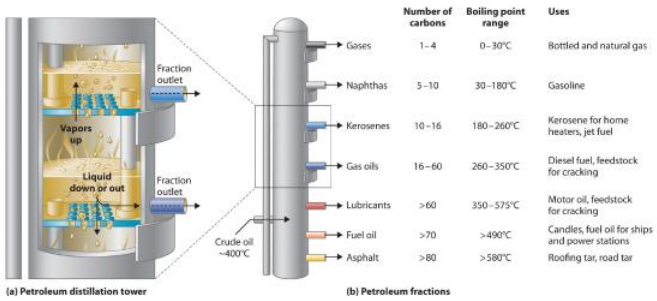


Figure 15.7.5: **The Distillation of Petroleum.** *(a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.*

The economics of petroleum refining are complex. For example, the market demand for kerosene and lubricants is much lower than the demand for gasoline, yet all three fractions are obtained from the distillation column in comparable amounts. Furthermore, most gasolines and jet fuels are blends with very carefully controlled compositions that cannot vary as their original feedstocks did. To make petroleum refining more profitable, the less volatile, lower-value fractions must be converted to more volatile, higher-value mixtures that have carefully controlled formulas. The first process used to accomplish this transformation is cracking, in which the larger and heavier hydrocarbons in the kerosene and higher-boiling-point fractions are heated to temperatures as high as 900°C. High-temperature reactions cause the carbon–carbon bonds to break, which converts the compounds to lighter molecules similar to those in the gasoline fraction. Thus in cracking, a straight-chain alkane with a number of carbon atoms corresponding to the

kerosene fraction is converted to a mixture of hydrocarbons with a number of carbon atoms corresponding to the lighter gasoline fraction. The second process used to increase the amount of valuable products is called reforming; it is the chemical conversion of straight-chain alkanes to either branched-chain alkanes or mixtures of aromatic hydrocarbons. Metal catalysts such as platinum are used to drive the necessary chemical reactions. The mixtures of products obtained from cracking and reforming are separated by fractional distillation.

Octane Ratings

The quality of a fuel is indicated by its octane rating, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure 15.8.6), which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

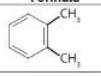
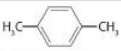
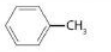
Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
n-heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0	*o*-xylene		107
n-hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
n-pentane	$CH_3CH_2CH_2CH_2CH_3$	62	*t*-butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	100	*p*-xylene		116
benzene		106	methyl *t*-butyl ether	$H_3COC(CH_3)_3$	116
methanol	CH_3OH	107	toluene		118

***Figure 15.76**: The Burning of Gasoline in an Internal Combustion Engine. (a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.*

The octane scale was established in 1927 using a standard test engine and two pure compounds: n-heptane and isooctane (2,2,4-trimethylpentane). n-Heptane, which causes a great deal of knocking on combustion, was assigned an octane rating of 0, whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100. Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of n-heptane and isooctane. For example, the octane rating of a blend of 89% isooctane and 11% n-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

$$0.89(100) + 0.11(0) = 89 \tag{4.7.1}$$

A gasoline that performs at the same level as a blend of 89% isooctane and 11% n-heptane is assigned an octane rating of 89; this represents an intermediate grade of gasoline. Regular gasoline typically has an octane rating of 87; premium has a rating of 93 or higher.

As shown in Figure 4.7.3, many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyllead [$(C_2H_5)_4Pb$], which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic.

Other enhancers, such as methyl t-butyl ether (MTBE), have been developed to take their place that combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

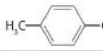
Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
n-heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0	*o*-xylene		107
n-hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
n-pentane	$CH_3CH_2CH_2CH_2CH_3$	62	*t*-butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	100	*p*-xylene		116
benzene		106	methyl *t*-butyl ether	$H_3COC(CH_3)_3$	116
methanol	CH_3OH	107	toluene		118

***Figure 15.7.6**: The Octane Ratings of Some Hydrocarbons and Common Additives*

Natural Gas

Natural gas is a (mostly) combustible gas found underground. While primarily composed of methane (70-90%) the gas from each well has a different composition and the value of the other components affects the value of the gas. The gas from wells that are rich in methane is called dry and wells that have a considerable amount of higher hydrocarbons produce wet gas. The higher hydrocarbons have value above that of methane so stripping them out is important. Some wells are sour because their gas has hydrogen sulfide which must be removed before the gas can be used for heating or generating electricity.

Finally, a few wells in Texas and nearby Oklahoma have a relatively high amount of helium (0.3 - 2.7%). The Helium Act of 1925 established a national helium reserve at Cliffside near Amarillo TX. Political pressure and costs pushed laws to privatize the reserve, but other policy considerations including the need for helium for scientific research has slowed the process.

Table 15.8.4: Composition of Natural Gas

Gas	Molecular Formula	Composition
Methane	CH_4	70-95%
Ethane	C_2H_6	0-20%
Carbon Dioxide	CO_2	0-8%
Nitrogen	N_2	0-5%
Hydrogen Sulfide	H_2S	0-5%
Propane	C_3H_8	Traces
Butane	C_4H_{10}	Traces
Rare Gases	He (also Ne)	0-3% (only in Texas)

The purification of natural gas is a complex process with many steps as each of the impurities is stripped out

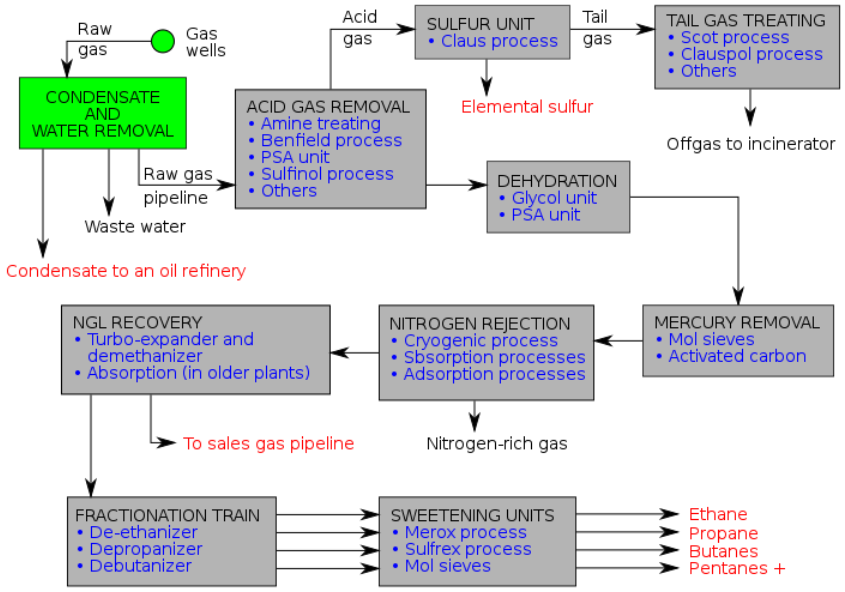


Figure 15.7.7: Purification of natural gas: *Prospective Chemical Engineers can find details about each process by searching the net. The flow chart is from the Wikipedia*

Gas turbine power plants to generate electricity are coming increasingly into use as fracking and other advanced drilling technologies have driven the cost of natural gas down and the supply up. While on a continental scale natural gas is transported by pipelines, natural gas can be cooled and compressed to be transported as liquified natural gas. Gas turbine power plants are small and quickly built. They can be rapidly spun up to meet peak demand. More detailed information can be found at the Department of Energy Fossil Fuel web site

The Carbon Cycle and the Greenhouse Effect

Since 1850 the burning of fossil fuels has increased the concentration of carbon dioxide in the atmosphere from 280 to just over 400 ppmV. A continued increase in the CO_2 burden in the atmosphere will have serious negative effects and this requires shifting our entire energy producing economy from fossil fuels to non-carbon sources such as hydro, solar, wind and nuclear. These include sea level rise that will threaten low lying cities including but not limited to Miami Beach and Norfolk in the US, even a meter or more coupled with storm surge and high tides can cause massive damage as was seen during Hurricane Sandy. Increased carbon dioxide in the atmosphere has already measurably decreased the pH of the oceans. Sea life is adapted to a narrow range of pH.

Higher global temperatures of 2 or 3 C may not seem much, but one should keep in mind that the average global temperature during the ice ages was only ~6 C lower than it is today. During the Eemian interglacial the average temperature was only a few degrees higher than the present and the sea level was 6-9 m higher. Finally, humans are mammals who maintain a core temperature within a few degrees of 37.0 C. In hot weather we do so by evaporation of sweat however there are limits to this and by 2100 there is a significant probability even in the US that at least a few days a year will reach this limit by 2100. Given that most people on earth do not have access to air conditioning, parts of the planet may become uninhabitable. Indeed a worst case and a serious problem that merits attention.

Given the constraints of this text it is difficult to provide the level of detail needed to understand why this is so. A good source for those interested in learning more is David Archer's Global Warming, Understanding the Forecast and An Introduction to Modern Climate Change by Andrew Dessler

There are a few basic facts that anyone starting to learn about the issue need to know. First, that the Earth gains energy from the Sun, and that it must radiate the energy at the same rate. If more energy is absorbed than radiated the Earth will warm up, if less energy is absorbed than radiated it will cool. As discussed in Section 15.1 solar radiation follows a 5500 K blackbody distribution while radiation from the surface of the earth is also black body but at ~290K. This is shown schematically in Figure 15.8.8

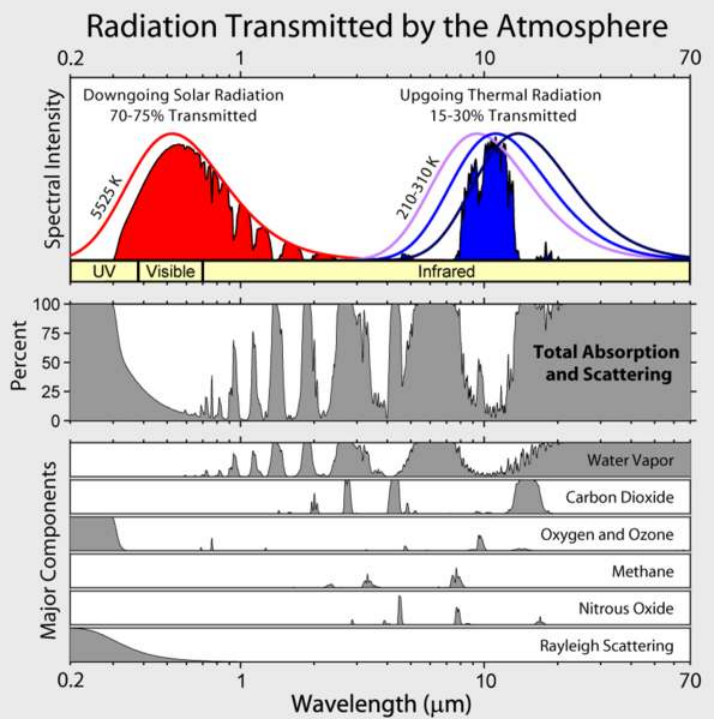


Figure 15.7.8: Origin of the greenhouse effect. *The top box show the intensity of solar radiation at the top of the Earth's atmosphere to the left and the infrared emission from the atmosphere to the left. The next shows the net absorption in the atmosphere across the spectrum. The bottom show the absorption by different atmospheric species at their current concentrations.* *Figure from the Wikipedia*

The atmosphere cools with altitude up to about 15 km where it starts warming again because of absorption of UV radiation by ozone in the stratosphere. The transition between the troposphere and the stratosphere is called the tropopause and is the coldest part of the atmosphere.

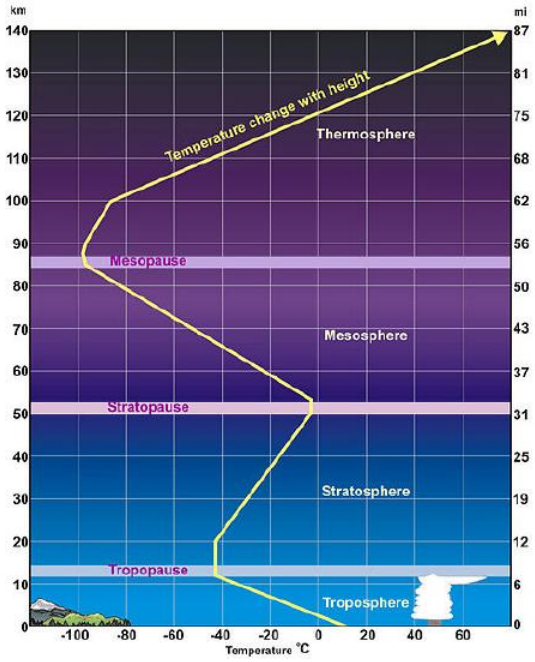


Figure 15.7.9 *The thermal structure of the atmosphere. The troposphere is the lowest level,extending from the the surface to the tropopause which is at 12-15 km altitude, more in the tropics and less less at the poles. The troposphere is the section of the*

atmosphere relevant to the greenhouse effect. The ozone layer is found in the stratosphere and one observes the aurora borealis or northern lights in the mesosphere Taken from Wikimedia

Figure 15.7.10 shows the IR emission spectrum observed looking down on the earth from a high altitude balloon

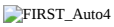


Figure 15.7.10: High resolution far infrared emission spectrum of the atmosphere looking down from a high altitude balloon at 35 km. *The strong band between 600 and 700 cm^{-1} is associated with CO_2, the sharp band at ~ 1100 cm^{-1} is associated with ozone and the feature near 1300 cm^{-1} is due to methane. The sharp lines (the hair) are due to water vapor. Spectrum is from the Federal Earth Observation Portal and was taken by an instrument operated by NASA/Langeley Research Center*

The dotted lines in Figure 15.8.9 are blackbody curves. The IR window shown schematically in blue in Figure 15.8.8 is the region between the ozone and the carbon dioxide band, where the emission from the hot, 320 K ground follows the blackbody curve with a few sharp water vapor absorption lines. At those wavelengths, in the IR window, the emission comes directly from the surface. The CO_2 band extends down to about a 220 K blackbody curve. What this means is that radiation from CO_2 only escapes to space from the level in the troposphere where that is the temperature. The rate of emission is proportional to T^4 so the rate of emission from higher, therefore colder levels, is slower. Radiation in this area of the spectrum from the surface is blocked and only the greatly reduced emission from the upper troposphere escapes to space. The same is true for the ozone and methane bands as well as the water lines.

The net effect is that the surface must warm in order to maintain the balance between incoming solar radiation and the outgoing emission. There is a simple calculation which models the atmosphere as a one dimensional problem and calculates what the temperature of the surface would be if there were no greenhouse gases. The result is 255 K, rather cold. In fact if one attempts a more complex calculation the effective temperature without greenhouse gases would be even colder.

What happens if we increase the carbon dioxide in the atmosphere? The altitude at which the atmosphere can emit radiation to space will rise because of increased absorption by the CO_2. Since in the troposphere the temperature decreases with altitude, the rate of emission from a higher level must decrease. Again, in order to maintain the balance between incoming solar radiation and the outgoing emission the surface will have to warm even more, thus the term global warming. The change is not linear with increasing CO_2 but logarithmic. But, of course it is not so simple, because increasing the surface temperature will increase the water vapor pressure in the atmosphere, which will increase the temperature further.

We also have to understand the flow of carbon between the atmosphere, the biosphere, the upper oceans and the deep. Observations to date show that natural emissions of CO_2 from these reservoirs are in balance with absorption, while only about half of fossil fuel emissions remain in the atmosphere, the rest being absorbed by the upper ocean and the biosphere. The three upper reservoirs equilibrate in a decade or less, but flow into the deep ocean requires roughly a thousand years.

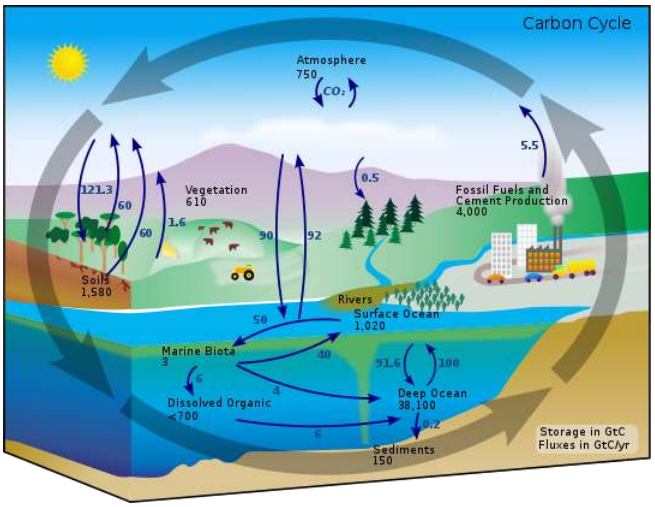


Figure 15.7.11: The carbon cycle. *Figure from the Wikipedia*

There is no doubt that atmospheric CO_2 levels are increasing, and the major reason for this increase is the combustion of fossil fuels. An extremely conservative statement of the situation today can be found in the 2014 Synthesis Report from the IPCC, a consensus between scientists and policymakers. The report starkly states that

> Cumulative emissions of CO_2 largely determine global mean surface warming by the late 21st century and beyond.

and concludes that

> Continued emission of greenhouse gases will cause further warming and long-lasting changes in all components of the climate system, increasing the likelihood of severe, pervasive and irreversible impacts for people and ecosystems. Limiting climate change would require substantial and sustained reductions in greenhouse gas emissions which, together with adaptation, can limit climate change risks.

The situation is serious, but we can work together to limit and even reverse damage while maintaining our standard of living in the developed world while helping the developing world to a better future. However, the issues are complex and we can only touch on some of the basics here.

Summary

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. Coal is primarily used for electricity generation. 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 results in increased surface temperatures (the **greenhouse effect**).

Key Takeaway

- Thermochemical concepts can be used to calculate the efficiency of various forms of fuel, which can then be applied to environmental issues.

Conceptual Problems

1. What is meant by the term *greenhouse gases*? List three greenhouse gases that have been implicated in global warming.
2. Name three factors that determine the rate of planetary CO_2 uptake.
3. The structure of coal is quite different from the structure of gasoline. How do their structural differences affect their enthalpies of combustion? Explain your answer.

Numerical Problems

1. One of the side reactions that occurs during the burning of fossil fuels is
   $4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$
   a. How many kilojoules of energy are released during the combustion of 10 lb of FeS_2?
   b. How many pounds of SO_2 are released into the atmosphere?
   c. Discuss the potential environmental impacts of this combustion reaction.
2. How many kilograms of CO_2 are released during the combustion of 16 gal of gasoline? Assume that gasoline is pure isooctane with a density of 0.6919 g/mL. If this combustion was used to heat 4.5×10^3 L of water from an initial temperature of 11.0°C, what would be the final temperature of the water assuming 42% efficiency in the energy transfer?
3. A 60 W light bulb is burned for 6 hours. If we assume an efficiency of 38% in the conversion of energy from oil to electricity, how much oil must be consumed to supply the electrical energy needed to light the bulb? (1 W = 1 J/s)

4. How many liters of cyclohexane must be burned to release as much energy as burning 10.0 lb of pine logs? The density of cyclohexane is 0.7785 g/mL, and its $\Delta H_{comb} = -46.6$ kJ/g.

Contributors

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8.2: Chemical Change



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8.3: Writing and Balancing Chemical Equations

Learning Objectives

- To describe a chemical reaction.
- To calculate the quantities of compounds produced or consumed in a chemical reaction

What happens to matter when it undergoes chemical changes? The Law of conservation of mass says that "***Atoms are neither created, nor destroyed, during any chemical reaction***." Thus, the same collection of atoms is present after a reaction as before the reaction. The changes that occur during a reaction just involve the *rearrangement* of atoms. In this section we will discuss ***stoichiometry*** (the "measurement of elements").

Chemical Equations

As shown in Figure 8.3.1, applying a small amount of heat to a pile of orange ammonium dichromate powder results in a vigorous reaction known as the ammonium dichromate volcano. Heat, light, and gas are produced as a large pile of fluffy green chromium(III) oxide forms. This reaction is described with a chemical equation, an expression that gives the identities and quantities of the substances in a chemical reaction.



Figure 8.3.1: An Ammonium Dichromate Volcano: Change during a Chemical Reaction. The starting material is solid ammonium dichromate. A chemical reaction transforms it to solid chromium(III) oxide, depicted showing a portion of its chained structure, nitrogen gas, and water vapor (in addition, energy in the form of heat and light is released). During the reaction, the distribution of atoms changes, but the number of atoms of each element does not change. Because the numbers of each type of atom are the same in the reactants and the products, the chemical equation is balanced. (CC BY-SA 3.0; Mikk Mihkel Vaabel via Wikipedia). See video here: www.youtube.com/watch?v=CW4hN0dYnkM

Chemical reactions are represented on paper by ***chemical equations***. For example, hydrogen gas (H_2) can react (burn) with oxygen gas (O_2) to form water (H_2O). The *chemical equation* for this *reaction* is written as:

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Chemical formulas and other symbols are used to indicate the starting materials, or reactants, which by convention are written on the left side of the equation, and the final compounds, or products, which are written on the right. An arrow points from the reactant to the products. The chemical reaction for the ammonium dichromate volcano in Figure 8.3.1 is

$$\underbrace{(NH_4)_2Cr_2O_7}_{reactant} \rightarrow \underbrace{Cr_2O_3 + N_2 + 4\,H_2O}_{products} \tag{8.3.1}$$

The arrow is read as “yields” or “reacts to form.” Equation 8.3.1 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:

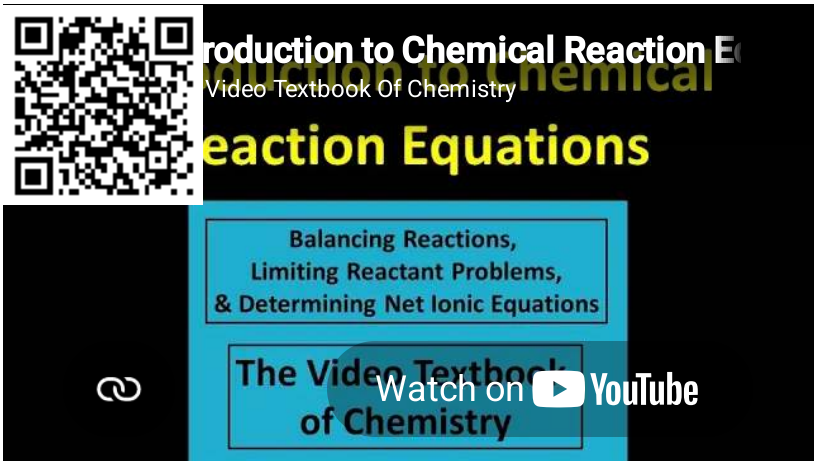
$$(NH_4)_2Cr_2O_7\,(s) \rightarrow Cr_2O_3\,(s) + N_2\,(g) + 4\,H_2O\,(g) \tag{8.3.2}$$

Equation 8.3.2 is identical to Equation 8.3.1 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 8.3.1 and 8.3.2. 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 8.3.1 and 8.3.2 are balanced chemical equations. What is different on each side of the equation is how the atoms are arranged to make molecules or ions. A chemical reaction represents a change in the distribution of atoms, but not in the number of atoms. In this reaction, and in most chemical reactions, bonds are broken in the reactants (here, Cr–O and N–H bonds), and new bonds are formed to create the products (here, O–H and N≡N bonds). If the numbers of each type of atom are different on the two sides of a chemical equation, then the equation is unbalanced, and it cannot correctly describe what happens during the reaction. To proceed, the equation must first be balanced.

A chemical reaction changes only the distribution of atoms, not the number of atoms.



Introduction to Chemical Reaction Equations: Introduction to Chemical Reaction Equations, YouTube(opens in new window) [youtu.be]

Balancing Simple Chemical Equations

When a chemist encounters a new reaction, it does not usually come with a label that shows the balanced chemical equation. Instead, the chemist must identify the reactants and products and then write them in the form of a chemical equation that may or may not be balanced as first written. Consider, for example, the combustion of n-heptane (C_7H_{16}), an important component of gasoline:

$$\mathrm{C_7H_{16}\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g)} \tag{8.3.3}$$

The complete combustion of any hydrocarbon with sufficient oxygen always yields carbon dioxide and water.



Figure 8.3.2: An Example of a Combustion Reaction. The wax in a candle is a high-molecular-mass hydrocarbon, which produces gaseous carbon dioxide and water vapor in a combustion reaction (Equation 8.3.3).

Equation 8.3.3 is not balanced: the numbers of each type of atom on the reactant side of the equation (7 carbon atoms, 16 hydrogen atoms, and 2 oxygen atoms) is not the same as the numbers of each type of atom on the product side (1 carbon atom, 2 hydrogen atoms, and 3 oxygen atoms). Consequently, the coefficients of the reactants and products must be adjusted to give the same numbers of atoms of each type on both sides of the equation. Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 8.3.3.

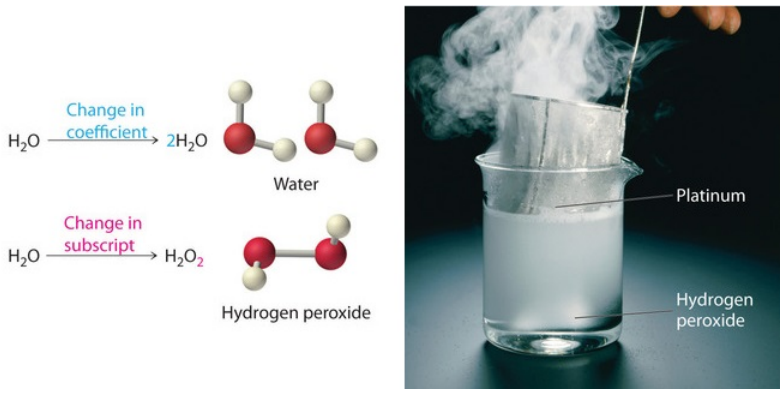
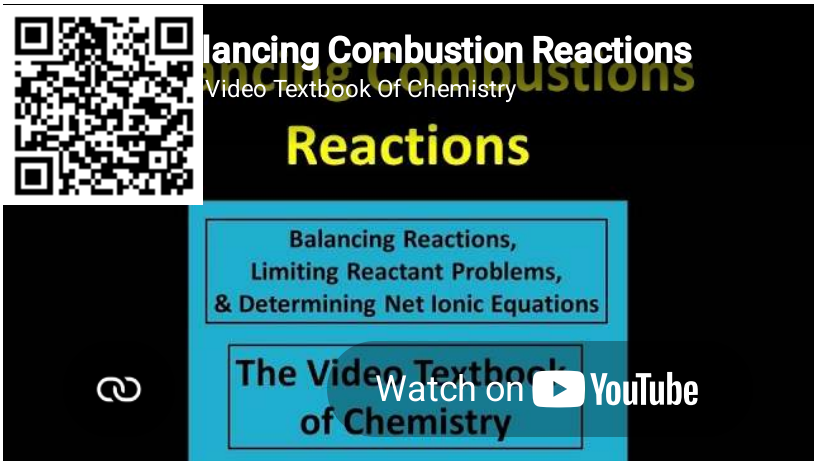


Figure 8.3.3: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

Left: Example of changing coefficients or subscripts. Right: Platinum dissolving in hydrogen peroxide.



Balancing Combustion Reactions: Balancing Combustions Reactions, YouTube(opens in new window) [youtu.be]

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element on both sides.
3. Balance polyatomic ions (if present) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Check your work by counting the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

Example 8.3.1A: Combustion of Heptane

To demonstrate this approach, let’s use the combustion of n-heptane (Equation 8.3.3) as an example.

1. **Identify the most complex substance**. The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.

2. **Adjust the coefficients**. Try to adjust the coefficients of the molecules on the other side of the equation to obtain the same numbers of atoms on both sides. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7\,CO_2 + H_2O \tag{8.3.4}$$

3. **Balance polyatomic ions as a unit**. There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms**. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H2O molecules, each of which contains 2 hydrogen atoms, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7\,CO_2 + 8\,H_2O \tag{8.3.5}$$

The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side:

$$C_7H_{16}\,(l) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g) \tag{8.3.6}$$

5. **Check your work**. The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start.

Example 8.3.1B: Combustion of Isooctane

Consider, for example, a similar reaction, the combustion of isooctane (C_8H_{18}). Because the combustion of any hydrocarbon with oxygen produces carbon dioxide and water, the unbalanced chemical equation is as follows:

$$C_8H_{18}\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g) \tag{8.3.7}$$

1. **Identify the most complex substance**. Begin the balancing process by assuming that the final balanced chemical equation contains a single molecule of isooctane.
2. **Adjust the coefficients**. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products:

$$C_8H_{18} + O_2 \rightarrow 8\,CO_2 + H_2O \tag{8.3.8}$$

3. **Balance polyatomic ions as a unit**. This step does not apply to this equation.
4. **Balance the remaining atoms**. Eighteen hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products:

$$C_8H_{18} + O_2 \rightarrow 8\,CO_2 + 9\,H_2O \tag{8.3.9}$$

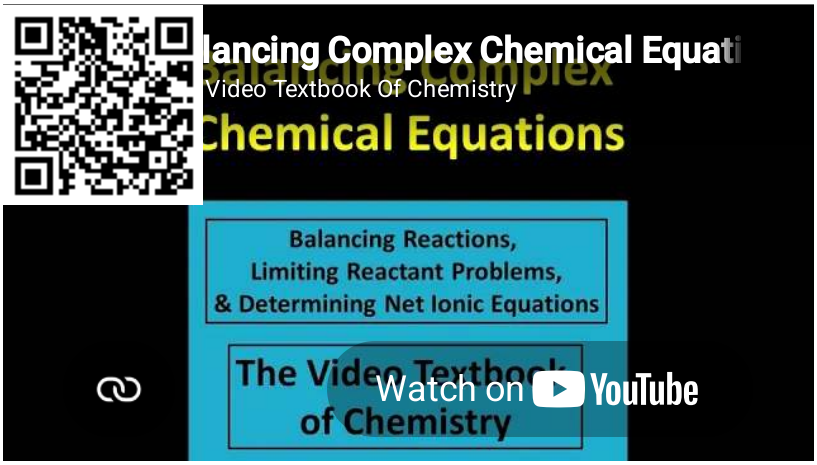
The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient (25/2) to balance the oxygen atoms:

$$C_8H_{18} + \tfrac{25}{2}\,O_2 \rightarrow 8\,CO_2 + 9\,H_2O \tag{8.3.10}$$

Equation 8.3.10 is now balanced, but we usually write equations with whole-number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by 2:

$$2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \rightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g) \tag{8.3.11}$$

5. **Check your work**. The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side.



Balancing Complex Chemical Equations: Balancing Complex Chemical Equations, YouTube(opens in new window) [youtu.be]

Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

Example $8.3.1C$: Hydroxyapatite

The reaction of the mineral hydroxyapatite ($Ca_5(PO_4)_3(OH)$) with phosphoric acid and water gives $Ca(H_2PO_4)_2 \cdot H_2O$ (calcium dihydrogen phosphate monohydrate). Write and balance the equation for this reaction.



Hydroxyapatite (Extra close brace or missing open brace) crystal

Given: reactants and product

Asked for: balanced chemical equation

Strategy:

A. Identify the product and the reactants and then write the unbalanced chemical equation.
B. Follow the steps for balancing a chemical equation.

Solution:

A We must first identify the product and reactants and write an equation for the reaction. The formulas for hydroxyapatite and calcium dihydrogen phosphate monohydrate are given in the problem (recall that phosphoric acid is H_3PO_4). The initial (unbalanced) equation is as follows:

$$Ca_5(PO_4)_3(OH)\,(s) + H_3PO_4\,(aq) + H_2O_{(l)} \rightarrow Ca(H_2PO_4)_2 \cdot H_2O_{(s)}$$

1. **B Identify the most complex substance**. We start by assuming that only one molecule or formula unit of the most complex substance, $Ca_5(PO_4)_3(OH)$, appears in the balanced chemical equation.

2. **Adjust the coefficients**. Because calcium is present in only one reactant and one product, we begin with it. One formula unit of $Ca_5(PO_4)_3(OH)$ contains 5 calcium atoms, so we need 5 $Ca(H_2PO_4)_2$•H_2O on the right side:

$$Ca_5(PO_4)_3(OH) + H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O$$

3. **Balance polyatomic ions as a unit**. It is usually easier to balance an equation if we recognize that certain combinations of atoms occur on both sides. In this equation, the polyatomic phosphate ion (PO_4^{3-}), shows up in three places. In H_3PO_4, the phosphate ion is combined with three H^+ ions to make phosphoric acid (H_3PO_4), whereas in $Ca(H_2PO_4)_2 \cdot H_2O$ it is combined with two H^+ ions to give the dihydrogen phosphate ion. Thus it is easier to balance PO_4 as a unit rather than counting individual phosphorus and oxygen atoms. There are 10 PO_4 units on the right side but only 4 on the left. The simplest way to balance the PO_4 units is to place a coefficient of 7 in front of H_3PO_4:

$$Ca_5(PO_4)_3(OH) + 7\,H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O$$

Although OH^- is also a polyatomic ion, it does not appear on both sides of the equation. So oxygen and hydrogen must be balanced separately.

4. **Balance the remaining atoms**. We now have 30 hydrogen atoms on the right side but only 24 on the left. We can balance the hydrogen atoms using the least complex substance, H_2O, by placing a coefficient of 4 in front of H_2O on the left side, giving a total of 4 H_2O molecules:

$$Ca_5(PO_4)_3(OH)\,(s) + 7\,H_3PO_4\,(aq) + 4\,H_2O\,(l) \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O\,(s)$$

The equation is now balanced. Even though we have not explicitly balanced the oxygen atoms, there are 41 oxygen atoms on each side.

5. **Check your work**. Both sides of the equation contain 5 calcium atoms, 10 phosphorus atoms, 30 hydrogen atoms, and 41 oxygen atoms.

? Exercise 8.3.1: Fermentation

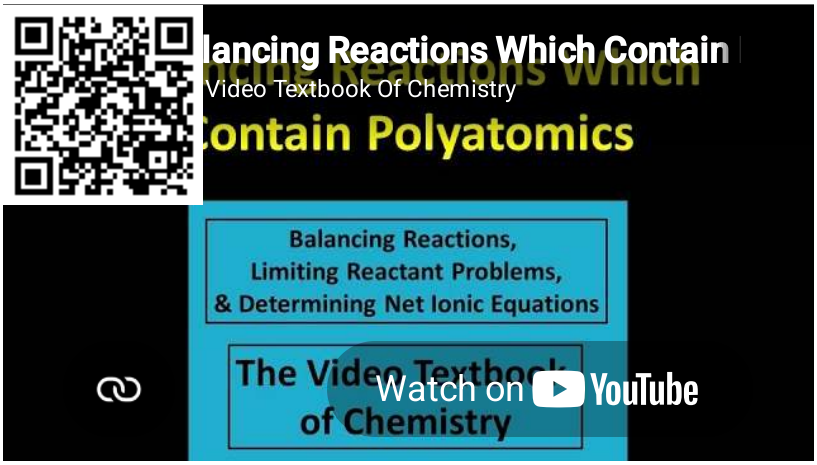
Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose are converted to ethanol (CH_3CH_2OH and carbon dioxide CO_2. Write a balanced chemical reaction for the fermentation of glucose.



***Commercial use of fermentation**. (a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.*

Answer

$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$



Balancing Reactions Which Contain Polyatomics: Balancing Reactions Which Contain Polyatomics, YouTube(opens in new window) [youtu.be]

Interpreting Chemical Equations

In addition to providing qualitative information about the identities and physical states of the reactants and products, a balanced chemical equation provides quantitative information. Specifically, it gives the relative amounts of reactants and products consumed or produced in a reaction. The number of atoms, molecules, or formula units of a reactant or a product in a balanced chemical equation is the coefficient of that species (e.g., the 4 preceding H_2O in Equation 8.3.1). When no coefficient is written in front of a species, the coefficient is assumed to be 1. As illustrated in Figure 8.3.4, the coefficients allow Equation 8.3.1 to be interpreted in any of the following ways:

- Two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion yield 1 formula unit of Cr_2O_3, 1 N_2 molecule, and 4 H_2O molecules.
- One mole of $(NH_4)_2Cr_2O_7$ yields 1 mol of Cr_2O_3, 1 mol of N_2, and 4 mol of H_2O.
- A mass of 252 g of $(NH_4)_2Cr_2O_7$ yields 152 g of Cr_2O_3, 28 g of N_2, and 72 g of H_2O.
- A total of 6.022×10^{23} formula units of $(NH_4)_2Cr_2O_7$ yields 6.022×10^{23} formula units of Cr_2O_3, 6.022×10^{23} molecules of N_2, and 24.09×10^{23} molecules of H_2O.

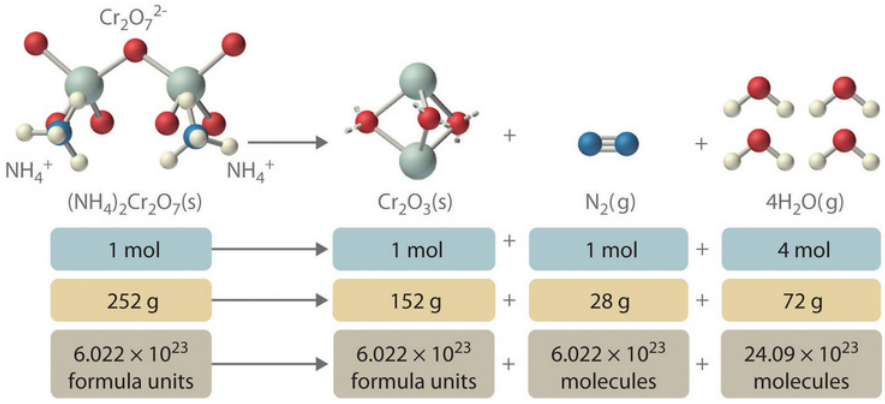


Figure 8.3.4: The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano

Chemical equation: (N H 4) 2 C r 2 O 7 dissociates into C r 2 O 3, N 2, and H 2 O. Conversions are given between moles, mass, and molecules.

These are all chemically equivalent ways of stating the information given in the balanced chemical equation, using the concepts of the mole, molar or formula mass, and Avogadro's number. The ratio of the number of moles of one substance to the number of moles of another is called the mole ratio. For example, the mole ratio of H_2O to N_2 in Equation 8.3.1 is 4:1. The total mass of reactants equals the total mass of products, as predicted by Dalton's law of conservation of mass:

$$252\ g \text{ of } (NH_4)_2Cr_2O_7$$

yield

$$152 + 28 + 72 = 252\ g \text{ of products.}$$

The chemical equation does not, however, show the rate of the reaction (rapidly, slowly, or not at all) or whether energy in the form of heat or light is given off. These issues are considered in more detail in later chapters.

An important chemical reaction was analyzed by Antoine Lavoisier, an 18th-century French chemist, who was interested in the chemistry of living organisms as well as simple chemical systems. In a classic series of experiments, he measured the carbon dioxide and heat produced by a guinea pig during respiration, in which organic compounds are used as fuel to produce energy, carbon dioxide, and water. Lavoisier found that the ratio of heat produced to carbon dioxide exhaled was similar to the ratio observed for the reaction of charcoal with oxygen in the air to produce carbon dioxide—a process chemists call combustion. Based on these experiments, he proposed that "Respiration is a combustion, slow it is true, but otherwise perfectly similar to that of charcoal." Lavoisier was correct, although the organic compounds consumed in respiration are substantially different from those found in charcoal. One of the most important fuels in the human body is glucose ($C_6H_{12}O_6$), which is virtually the only fuel used in the brain. Thus combustion and respiration are examples of chemical reactions.

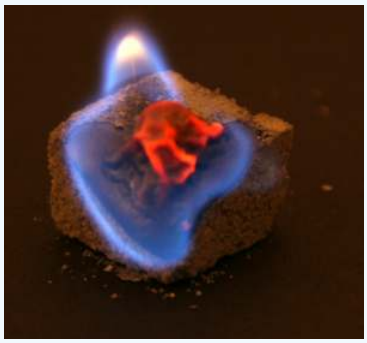
Example 8.3.2: Combustion of Glucose

The balanced chemical equation for the combustion of glucose in the laboratory (or in the brain) is as follows:

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

Construct a table showing how to interpret the information in this equation in terms of

a. a single molecule of glucose.
b. moles of reactants and products.
c. grams of reactants and products represented by 1 mol of glucose.
d. numbers of molecules of reactants and products represented by 1 mol of glucose.



The combustion of a sugar cube consisting of sucrose with a similar reaction to the combustion of glucose. from Wikipedia.

Given: balanced chemical equation

Asked for: molecule, mole, and mass relationships

Strategy:

A. Use the coefficients from the balanced chemical equation to determine both the molecular and mole ratios.
B. Use the molar masses of the reactants and products to convert from moles to grams.
C. Use Avogadro's number to convert from moles to the number of molecules.

Solution:

This equation is balanced as written: each side has 6 carbon atoms, 18 oxygen atoms, and 12 hydrogen atoms. We can therefore use the coefficients directly to obtain the desired information.

a. One molecule of glucose reacts with 6 molecules of O_2 to yield 6 molecules of CO_2 and 6 molecules of H_2O.
b. One mole of glucose reacts with 6 mol of O_2 to yield 6 mol of CO_2 and 6 mol of H_2O.

c. To interpret the equation in terms of masses of reactants and products, we need their molar masses and the mole ratios from part b. The molar masses in grams per mole are as follows: glucose, 180.16; O_2, 31.9988; CO_2, 44.010; and H_2O, 18.015.

$$\text{mass of reactants} = \text{mass of products}$$

$$g\,glucose + g\,O_2 = g\,CO_2 + g\,H_2O$$

$$1\,mol\,glucose\left(\frac{180.16\,g}{1\,mol\,glucose}\right) + 6\,mol\,O_2\left(\frac{31.9988\,g}{1\,mol\,O_2}\right)$$

$$= 6\,mol\,CO_2\left(\frac{44.010\,g}{1\,mol\,CO_2}\right) + 6\,mol\,H_2O\left(\frac{18.015\,g}{1\,mol\,H_2O}\right)$$

$$372.15\,g = 372.15\,g$$

C One mole of glucose contains Avogadro's number (6.022×10^{23}) of glucose molecules. Thus 6.022×10^{23} glucose molecules react with ($6 \times 6.022 \times 10^{23}$) = 3.613×10^{24} oxygen molecules to yield ($6 \times 6.022 \times 10^{23}$) = 3.613×10^{24} molecules each of CO_2 and H_2O.

In tabular form:

Solution to Example 3.1.2

	$C_6H_{12}O_{6\ (s)}$	+	$6O_{2\ (g)}$	→	$6CO_{2\ (g)}$		$6H_2O_{(l)}$
a.	1 molecule		6 molecules		6 molecules		6 molecules
b.	1 mol		6 mol		6 mol		6 mol
c.	180.16 g		191.9928 g		264.06 g		108.09 g
d.	6.022×10^{23} molecules		3.613×10^{24} molecules		3.613×10^{24} molecules		3.613×10^{24} molecule

? Exercise 8.3.2: Ammonium Nitrate Explosion

Ammonium nitrate is a common fertilizer, but under the wrong conditions it can be hazardous. In 1947, a ship loaded with ammonium nitrate caught fire during unloading and exploded, destroying the town of Texas City, Texas.



Ammonium nitrate can be hazardous. This aerial photograph of Texas City, Texas, shows the devastation caused by the explosion of a shipload of ammonium nitrate on April 16, 1947. For a video click here.

The explosion resulted from the following reaction:

$$2NH_4NO_{3\ (s)} \rightarrow 2N_{2\ (g)} + 4H_2O_{(g)} + O_{2\ (g)}$$

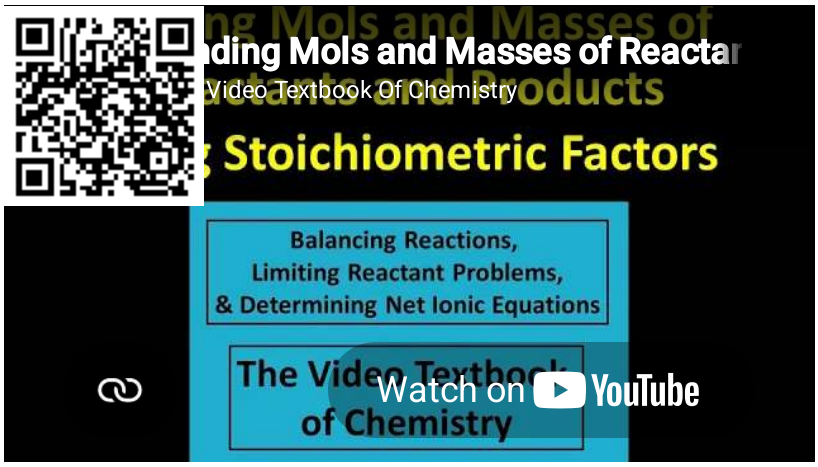
Construct a table showing how to interpret the information in the equation in terms of

a. individual molecules and ions.
b. moles of reactants and products.
c. grams of reactants and products given 2 mol of ammonium nitrate.
d. numbers of molecules or formula units of reactants and products given 2 mol of ammonium nitrate.

Answer:

Answer to Exercise 3.1.2

	$2NH_4NO_{3\ (s)}$	→	$2N_{2\ (g)}$	+	$4H_2O_{(g)}$	+	$O_{2\ (g)}$
a.	$2NH_4^+$ ions and $2NO_3^-$ ions		2 molecules		4 molecules		1 molecule
b.	2 mol		2 mol		4 mol		1 mol
c.	160.0864 g		56.0268 g		72.0608 g		31.9988 g
d.	1.204×10^{24} formula units		1.204×10^{24} molecules		2.409×10^{24} molecules		6.022×10^{23} molecules



Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors (Mol Ratios): Finding Mols and Masses of Reactants and Products Using Stoichiometric Factors, YouTube(opens in new window) [youtu.be]

Summary

A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products. In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a **chemical equation**, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the **reactants**—on the left and the final compound(s)—the **products**—on the right, separated by an arrow. In a balanced chemical equation, the numbers of atoms of each element and the total charge are the same on both sides of the equation. The number of atoms, molecules, or formula units of a reactant or product in a balanced chemical equation is the **coefficient** of that species. The **mole ratio** of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.

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8.4: Reaction Stoichiometry - How Much Carbon Dioxide?

Learning Objectives

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's stoichiometry, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Cooking, for example, offers an appropriate comparison. Suppose a recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$1 \text{ cup mix} + \frac{3}{4} \text{ cup milk} + 1 \text{ egg} \rightarrow 8 \text{ pancakes} \tag{8.4.1}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \ \cancel{\text{pancakes}} \times \frac{1 \text{ egg}}{8 \ \cancel{\text{pancakes}}} = 3 \text{ eggs} \tag{8.4.2}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive stoichiometric factors that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g) \tag{8.4.3}$$

This equation shows that ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2 NH3\ molecules}{3 H2\ molecules} \text{ or } \frac{2\ doz\ NH3\ molecules}{3\ doz\ H2\ molecules} \text{ or } \frac{2\ mol\ NH3\ molecules}{3\ mol\ H2\ molecules} \tag{8.4.4}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 8.4.1: Moles of Reactant Required in a Reaction

How many moles of $\mathrm{I_2}$ are required to react with 0.429 mol of Al according to the following equation (see Figure 8.4.2)?

$$2\,\mathrm{Al} + 3\,\mathrm{I_2} \rightarrow 2\,\mathrm{AlI_3} \tag{8.4.5}$$

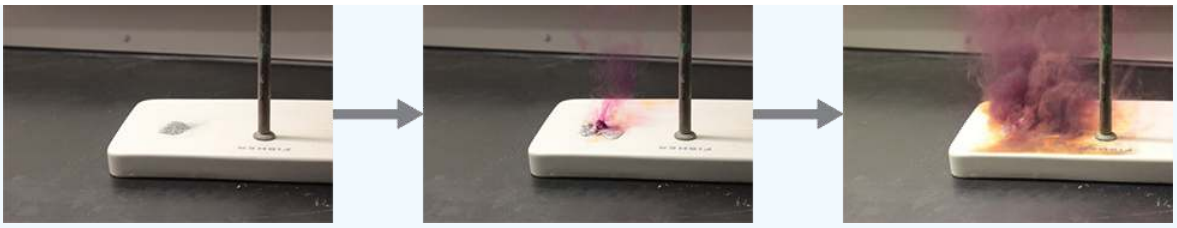
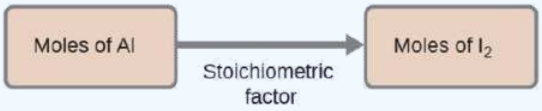


Figure 8.4.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Three pictures showing the progression of the reaction between iodine and aluminum. The first diagram shows only a pile of silver powder while the second diagram shows small amount of vapor forming. The final picture shows a large release of purple vapor.

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3\ mol\ I2}{2\ mol\ Al}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\text{mol I}_2 = 0.429\ \cancel{\text{mol Al}} \times \frac{3\ \text{mol I}_2}{2\ \cancel{\text{mol Al}}}$$

$$= 0.644\ \text{mol I}_2$$

Exercise 8.4.1

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3\,Ca(OH)_2 + 2\,H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\,H_2O$?

Answer

2.04 mol

Example 8.4.2: Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \tag{8.4.6}$$

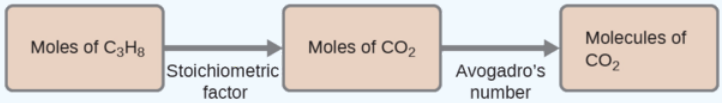
Solution

The approach here is the same as for Example 8.4.1, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

\[\ce{\dfrac{3\: mol\: CO2}{1\: mol\: C3H8}} \label{4.4.7} \]

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75\ \cancel{\text{mol C}_3\text{H}_8} \times \frac{3\ \cancel{\text{mol CO}_2}}{1\ \cancel{\text{mol C}_3\text{H}_8}} \times \frac{6.022 \times 10^{23}\ \text{CO}_2\ \text{molecules}}{\cancel{\text{mol CO}_2}} \tag{8.4.7}$$

$$= 1.4 \times 10^{24}\ \text{CO}_2\ \text{molecules}$$

Exercise 8.4.1

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2\,NH_3 + CaSO_4 + 2\,H_2O \tag{8.4.8}$$

Answer

4.8×10^{24} NH_3 molecules

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

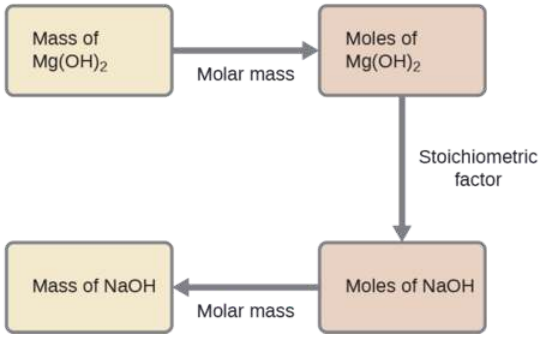
Example 8.4.3: Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$MgCl_2(aq) + 2\,NaOH(aq) \rightarrow Mg(OH)_2(s) + 2\,NaCl(aq)$$

Solution

The approach used previously in Examples 8.4.1 and 8.4.2 is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



$$16\ \cancel{\text{g Mg(OH)}_2} \times \frac{1\ \cancel{\text{mol Mg(OH)}_2}}{58.3\ \cancel{\text{g Mg(OH)}_2}} \times \frac{2\ \cancel{\text{mol NaOH}}}{1\ \cancel{\text{mol Mg(OH)}_2}} \times \frac{40.0\ \text{g NaOH}}{\cancel{\text{mol NaOH}}} = 22\ \text{g NaOH}$$

Exercise 8.4.3

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4\,Ga + 3\,O_2 \rightarrow 2\,Ga_2O_3$.

Answer

39.0 g

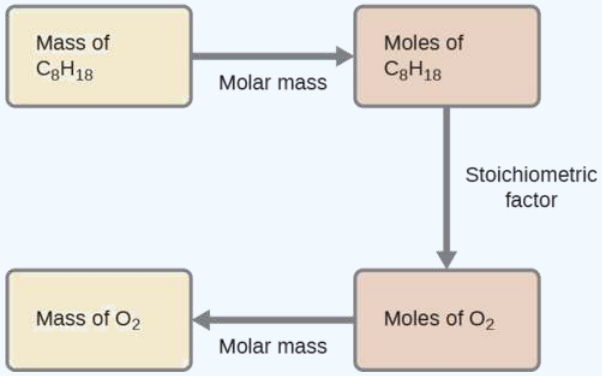
Example 8.4.4: Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$$

Solution

The approach required here is the same as for the Example 8.4.3, differing only in that the provided and requested masses are both for reactant species.



$$702\ \cancel{\text{g C}_8\text{H}_{18}} \times \frac{1\ \cancel{\text{mol C}_8\text{H}_{18}}}{114.23\ \cancel{\text{g C}_8\text{H}_{18}}} \times \frac{25\ \cancel{\text{mol O}_2}}{2\ \cancel{\text{mol C}_8\text{H}_{18}}} \times \frac{32.00\ \text{g O}_2}{\cancel{\text{mol O}_2}} = 2.46 \times 10^3\ \text{g O}_2$$

? Exercise 8.4.4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $\text{Fe}_2\text{O}_3 + 3\,\text{CO} \rightarrow 2\,\text{Fe} + 3\,\text{CO}_2$?

Answer

13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure 8.4.2 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

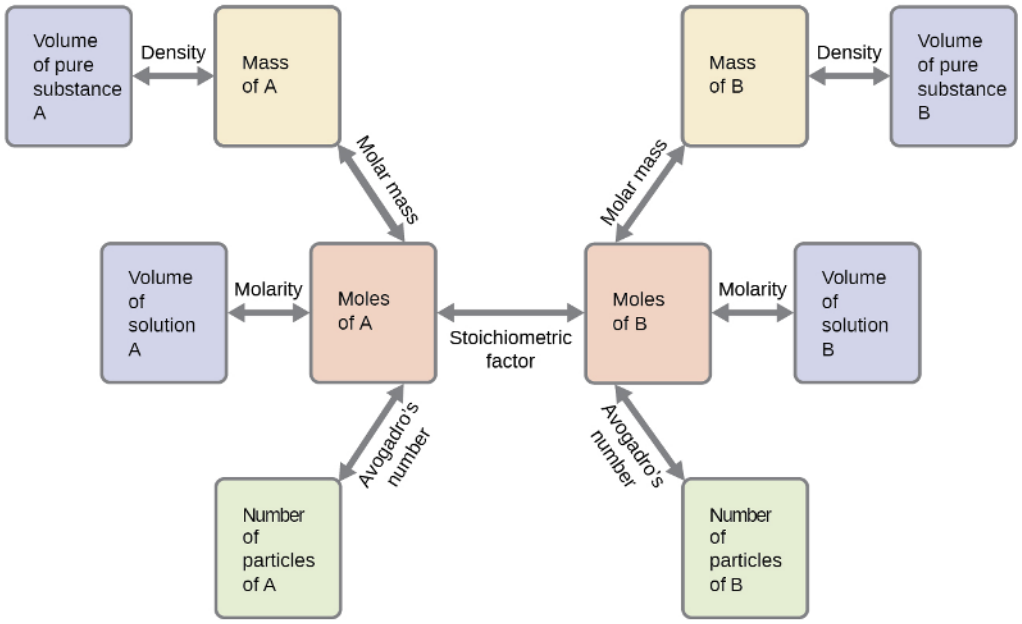


Figure 8.4.2: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Schematic flowchart showing how density is used for converting volume of pure substance to mass, molar mass for mass and moles, molarity for moles and volume of solution, Avogadro's number for moles and number of particles, and stoichiometric factor for relating moles of one substance to another.

Airbags

Airbags (Figure 8.4.3) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,NaN_3(s) \rightarrow 3\,N_2(g) + 2\,Na(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure 8.4.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Summary

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

Glossary

stoichiometric factor

ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry

relationships between the amounts of reactants and products of a chemical reaction

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8.5: Limiting Reactant, Theoretical Yield, and Percent Yield

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

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{8.5.1}$$

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.

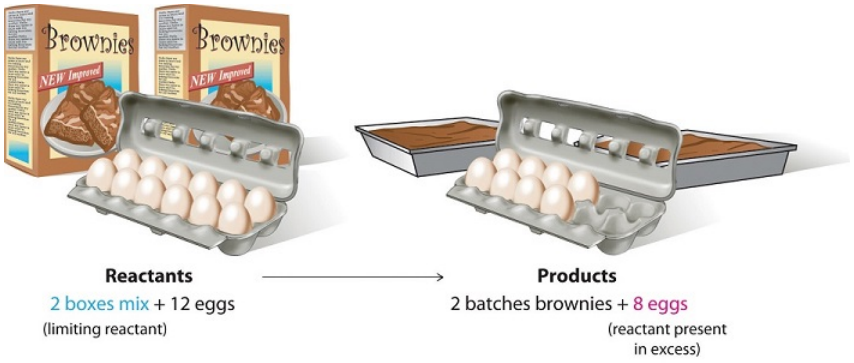
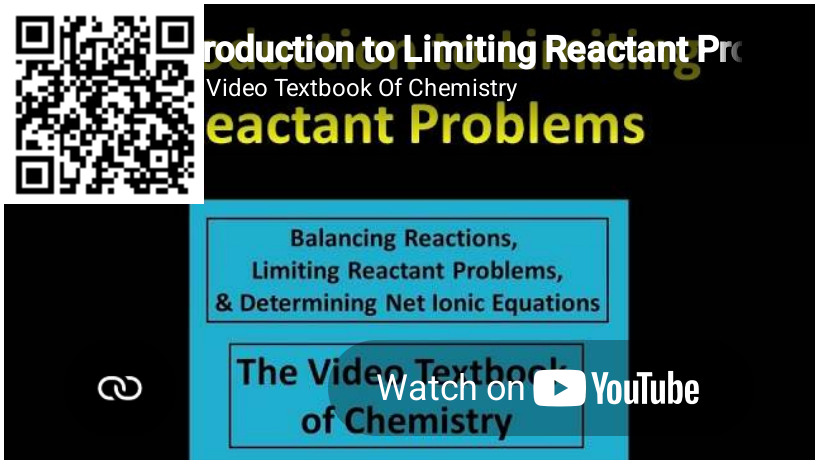


Figure 8.5.1: The Concept of a Limiting Reactant in the Preparation of Brownies

Reactants: 2 boxes of brownie mix + 12 eggs produces 2 batches of brownies + 8 eggs. Brownie mix is the limiting reactant. Eggs are the reactant present in excess.



Introduction to Limiting Reactant Problems: Introduction to Limiting Reactant Problems, YouTube(opens in new window) [youtu.be]

Now consider a chemical example of a limiting reactant: the production of pure titanium. This metal is fairly light (45% lighter than steel and only 60% heavier than aluminum) and has great mechanical strength (as strong as steel and twice as strong as aluminum). Because it is also highly resistant to corrosion and can withstand extreme temperatures, titanium has many applications in the aerospace industry. Titanium is also used in medical implants and portable computer housings because it is light and resistant to corrosion. Although titanium is the ninth most common element in Earth's crust, it is relatively difficult to extract from its ores. In the first step of the extraction process, titanium-containing oxide minerals react with solid carbon and chlorine gas to form titanium tetrachloride ($\mathrm{TiCl_4}$) and carbon dioxide.

$$\mathrm{TiO_2\,(s) + Cl_2\,(g)\ \rightarrow TiCl_4\,(g) + CO_2\,(g)}$$

Titanium tetrachloride is then converted to metallic titanium by reaction with molten magnesium metal at high temperature:

$$\mathrm{TiCl_4\,(g) + 2\ Mg\,(l)\ \rightarrow Ti\,(s) + 2\ MgCl_2\,(l)} \tag{8.5.2}$$

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 8.5.2: Medical use of titanium. Here is an example of its successful use in joint replacement implants. An A-P X-ray of a pelvis showing a total hip joint replacement. The right hip joint (on the left in the photograph) has been replaced. A metal prostheses is cemented in the top of the right femur and the head of the femur has been replaced by the rounded head of the prosthesis. Figure courtesy of NIH (NIADDK) 9AO4 (Connie Raab)

With 1.00 kg of titanium tetrachloride and 200 g of magnesium metal, how much titanium metal can be produced according to Equation 8.5.2?

Solving this type of problem requires that you carry out the following steps

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.
4. Convert the number of moles of product to mass of product.

Step 1: To determine the number of moles of reactants present, calculate or look up their molar masses: 189.679 g/mol for titanium tetrachloride and 24.305 g/mol for magnesium. The number of moles of each is calculated as follows:

$$\begin{aligned}\text{moles TiCl}_4 &= \frac{\text{mass TiCl}_4}{\text{molar mass TiCl}_4} \\ &= 1000 \cancel{g}\ \text{TiCl}_4 \times \frac{1\, mol\ TiCl_4}{189.679 \cancel{g}\ \text{TiCl}_4} \\ &= 5.272\, mol\ \text{TiCl}_4 \end{aligned} \tag{8.5.3}$$

$$\begin{aligned}\text{moles Mg} &= \frac{\text{mass Mg}}{\text{molar mass Mg}} \\ &= 200 \cancel{g}\ \text{Mg} \times \frac{1\, mol\, \text{Mg}}{24.305 \cancel{g}\ \text{Mg}} \\ &= 8.23\, \text{mol Mg} \end{aligned} \tag{8.5.4}$$

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

$$\frac{mol\, \text{Mg}}{mol\, \text{TiCl}_4} = \frac{8.23\, mol}{5.272\, mol} = 1.56$$

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

$$\frac{2\, mol\, \text{Mg}}{1\, mol\, \text{TiCl}_4} = 2$$

there is not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear from the mole ratio, calculate the number of moles of one reactant that is required for complete reaction of the other reactant. For example, there are 8.23 mol of Mg, so (8.23 ÷ 2) = 4.12 mol of 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.

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

$$mol\ \text{Ti} = 8.23\, mol\ \text{Mg} = \frac{1\, mol\ \text{Ti}}{2\, mol\ \text{Mg}} = 4.12\, mol\ \text{Ti}$$

Thus only 4.12 mol of Ti can be formed.

Step 4. To calculate the mass of titanium metal that can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

$$\begin{aligned}\text{moles Ti} &= \text{mass Ti} \times \text{molar mass Ti} \\ &= 4.12\, mol\ \text{Ti} \times \frac{47.867\, g\ \text{Ti}}{1\, mol\ \text{Ti}} \\ &= 197\, g\ \text{Ti} \end{aligned}$$

Here is a simple and reliable way to identify the limiting reactant in any problem of this sort:

1. Calculate the number of moles of each reactant present: 5.272 mol of TiCl_4 and 8.23 mol of Mg.
2. Divide the actual number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation:

$$TiCl_4 : \frac{5.272\, mol\, (actual)}{1\, mol\, (stoich)} = 5.272$$

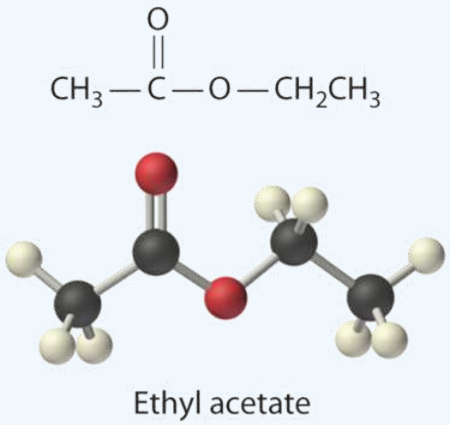
$$Mg : \frac{8.23\, mol\, (actual)}{2\, mol\, (stoich)} = 4.12$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

Density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example 8.5.1 demonstrates.

Example 8.5.1: 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.



Ethyl acetate

Given: reactants, products, and volumes and densities of reactants

Asked for: mass of product

Strategy:

A. Balance the chemical equation for the reaction.
B. Use the given densities to convert from volume to mass. Then use each molar mass to convert from mass to moles.
C. Using mole ratios, determine which substance is the limiting reactant. After identifying the limiting reactant, use mole ratios based on the number of moles of limiting reactant to determine the number of moles of product.
D. Convert from moles of product to mass of product.

Solution:

A Always begin by writing the balanced chemical equation for the reaction:

$$C_2H_5OH\,(l) + CH_3CO_2H\,(aq) \rightarrow CH_3CO_2C_2H_5\,(aq) + H_2O\,(l)$$

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

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

Rearranging this expression gives mass = (density)(volume). We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 cm^3):

$$\begin{aligned}\text{moles } C_2H_5OH &= \frac{\text{mass } C_2H_5OH}{\text{molar mass } \ C_2H_5OH}\\ &= \frac{(\text{volume } C_2H_5OH) \times (\text{density } C_2H_5OH)}{\text{molar mass } \ C_2H_5OH}\\ &= 10.0 \cancel{ml}\ {}_2CH_5OH \times \frac{0.7893 \cancel{g}\ C_2H_5OH}{1 \cancel{ml}\ C_2H_5OH} \times \frac{1\, mol\ C_2H_5OH}{46.07 \cancel{g}\ C_2H_5OH}\\ &= 0.171\, mol\ {}_2CH_5OH\\ \text{moles } CH_3CO_2H &= \frac{\text{mass } CH_3CO_2H}{\text{molar mass } CH_3CO_2H}\\ &= \frac{(\text{volume } CH_3CO_2H) \times (\text{density } CH_3CO_2H)}{\text{molar mass } CH_3CO_2H}\\ &= 10.0 \cancel{ml}\ CH_3CO_2H \times \frac{1.0492 \cancel{g}\ CH_3CO_2H}{1 \cancel{ml}\ CH_3CO_2H} \times \frac{1\, mol\ CH_3CO_2H}{60.05 \cancel{g}\ CH_3CO_2H}\\ &= 0.175\, mol\ CH_3CO_2H\end{aligned}$$

C The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

$$\begin{aligned}moles \text{ ethyl acetate} &= mol \text{ ethanol} \times \frac{1\, mol \text{ ethyl acetate}}{1\, mol \text{ ethanol}}\\ &= 0.171\, mol\ {}_2CH_5OH \times \frac{1\, mol\, CH_3CO_2C_2H_5}{1\, mol\ C_2H_5OH}\\ &= 0.171\, mol\ {}_{322}CHCOCH_5\end{aligned}$$

D The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

$$\begin{aligned}\text{mass of ethyl acetate} &= mol \text{ ethyl acetate} \times \text{molar mass ethyl acetate}\\ &= 0.171\, mol\ {}_{322}CHCOCH_5 \times \frac{88.11\, g\, CH_3CO_2C_2H_5}{1\, mol\, CH_3CO_2C_2H_5}\\ &= 15.1\, g\, CH_3CO_2C_2H_5\end{aligned}$$

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm3) to determine the volume of ethyl acetate that could be produced:

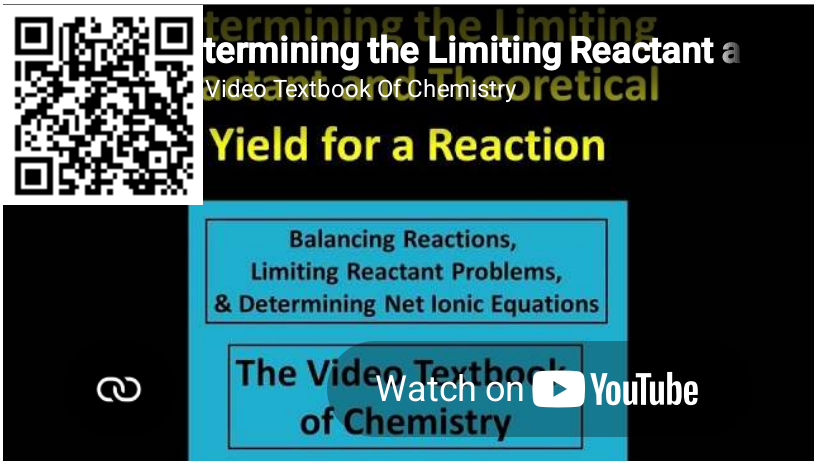
$$\begin{aligned}\text{volume of ethyl acetate} &= 15.1\, g\, CH_3CO_2C_2H_5 \times \frac{1\, ml\ CH_3CO_2C_2H_5}{0.9003\, g\ CH_3CO_2C_2H_5}\\ &= 16.8\, ml\ {}_{322}CHCOCH_5\end{aligned}$$

? Exercise 8.5.1

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



Determining the Limiting Reactant and Theoretical Yield for a Reaction: Determining the Limiting Reactant and Theoretical Yield for a Reaction, YouTube(opens in new window) [youtu.be]

Limiting Reactants in Solutions

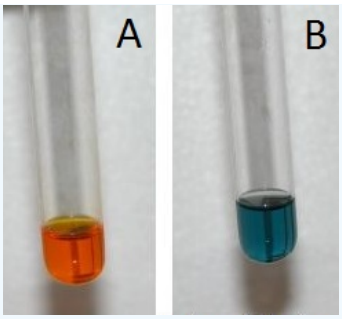
The concept of limiting reactants applies to reactions carried out in solution as well as to reactions involving pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 8.5.2.

Example 8.5.2: Breathalyzer reaction

Because the consumption of alcoholic beverages adversely affects the performance of tasks that require skill and judgment, in most countries it is illegal to drive while under the influence of alcohol. In almost all US states, a blood alcohol level of 0.08% by volume is considered legally drunk. Higher levels cause acute intoxication (0.20%), unconsciousness (about 0.30%), and even death (about 0.50%). The Breathalyzer is a portable device that measures the ethanol concentration in a person's breath, which is directly proportional to the blood alcohol level. The reaction used in the Breathalyzer is the oxidation of ethanol by the dichromate ion:

$$3\,\mathrm{CH_3\ CH_2\ OH\,(aq)} + 2\underset{yellow-orange}{\mathrm{Cr_2\ O_7^{2-}}}(aq) + 16\,\mathrm{H^+\,(aq)} \xrightarrow[\mathrm{H_2SO_4\,(aq)}]{\mathrm{Ag^+}} 3\,\mathrm{CH_3CO_2H\,(aq)} + 4\underset{green}{\mathrm{Cr^{3+}}}(aq) + 11\,\mathrm{H_2O\,(l)}$$

When a measured volume (52.5 mL) of a suspect's breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $Cr_2O_7^{2-}$ ions are reduced from Cr^{6+} to Cr^{3+}. In the presence of Ag^+ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $Cr_2O_7^{2-}$ ion (the reactant) is yellow-orange and the Cr^{3+} ion (the product) forms a green solution, the amount of ethanol in the person's breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.



A Breathalyzer reaction with a test tube before (a) and after (b) ethanol is added. When a measured volume of a suspect's breath is bubbled through the solution, the ethanol is oxidized to acetic acid, and the solution changes color from yellow-orange to green. The intensity of the green color indicates the amount of ethanol in the sample.

A typical Breathalyzer ampul contains 3.0 mL of a 0.25 mg/mL solution of $K_2Cr_2O_7$ in 50% H_2SO_4 as well as a fixed concentration of $AgNO_3$ (typically 0.25 mg/mL is used for this purpose). How many grams of ethanol must be present in 52.5 mL of a person's breath to convert all the Cr^{6+} to Cr^{3+}?

Given: volume and concentration of one reactant

Asked for: mass of other reactant needed for complete reaction

Strategy:

A. Calculate the number of moles of $Cr_2O_7^{2-}$ ion in 1 mL of the Breathalyzer solution by dividing the mass of $K_2Cr_2O_7$ by its molar mass.

B. Find the total number of moles of $Cr_2O_7^{2-}$ ion in the Breathalyzer ampul by multiplying the number of moles contained in 1 mL by the total volume of the Breathalyzer solution (3.0 mL).

C. Use the mole ratios from the balanced chemical equation to calculate the number of moles of C_2H_5OH needed to react completely with the number of moles of $Cr_2O_7^{2-}$ ions present. Then find the mass of C_2H_5OH needed by multiplying the number of moles of C_2H_5OH by its molar mass.

Solution:

A In any stoichiometry problem, the first step is always to calculate the number of moles of each reactant present. In this case, we are given the mass of $K_2Cr_2O_7$ in 1 mL of solution, which can be used to calculate the number of moles of $K_2Cr_2O_7$ contained in 1 mL:

$$\frac{moles\ K_2Cr_2O_7}{1\ mL} = \frac{(0.25\ \cancel{mg}\ K_2Cr_2O_7)}{mL}\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{294.18\ \cancel{g}\ K_2Cr_2O_7}\right) = 8.5 \times 10^{-7}\ moles$$

B Because 1 mol of $K_2Cr_2O_7$ produces 1 mol of $Cr_2O_7^{2-}$ when it dissolves, each milliliter of solution contains 8.5×10^{-7} mol of $Cr_2O_7^{2-}$. The total number of moles of $Cr_2O_7^{2-}$ in a 3.0 mL Breathalyzer ampul is thus

$$moles\ Cr_2O_7^{2-} = \left(\frac{8.5 \times 10^{-7}\ mol}{1\ \cancel{mL}}\right)(3.0\ \cancel{mL}) = 2.6 \times 10^{-6}\ mol\ Cr_2O_7^{2-}$$

C The balanced chemical equation tells us that 3 mol of C_2H_5OH is needed to consume 2 mol of $Cr_2O_7^{2-}$ ion, so the total number of moles of C_2H_5OH required for complete reaction is

$$moles\ of\ C_2H_5OH = (2.6 \times 10^{-6}\ \cancel{mol\ Cr_2O_7^{2-}})\left(\frac{3\ mol\ C_2H_5OH}{2\ \cancel{mol\ Cr_2O_7^{2-}}}\right)$$
$$= 3.9 \times 10^{-6}\ mol\ {}_2CH_5OH$$

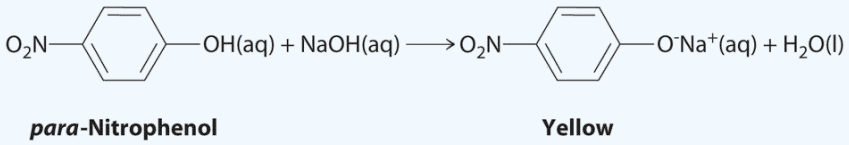
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ {}_2CH_5OH = (3.9 \times 10^{-6}\ \cancel{mol\ {}_2CH_5OH}) \left(\frac{46.07\ g}{\cancel{mol\ {}_2CH_5OH}} \right) = 1.8 \times 10^{-4}\ g\ C_2H_5OH$$

Thus 1.8×10^{-4} g or 0.18 mg of C_2H_5OH must be present. Experimentally, it is found that this value corresponds to a blood alcohol level of 0.7%, which is usually fatal.

Exercise 8.5.2

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction



para-Nitrophenol **Yellow**

Chemical equation showing conversion of para-nitrophenol to its yellow-colored form with aqueous sodium hydroxide.

Because the amount of *para*-nitrophenol is easily estimated from the intensity of the yellow color that results when excess NaOH is added, reactions that produce *para*-nitrophenol are commonly used to measure the activity of enzymes, the catalysts in biological systems. What volume of 0.105 M NaOH must be added to 50.0 mL of a solution containing 7.20×10^{-4} g of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

Answer

4.93×10^{-5} L or 49.3 µL

In Examples 8.5.1 and 8.5.2, 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 8.5.3.

Example 8.5.3

When aqueous solutions of silver nitrate and potassium dichromate are mixed, an exchange reaction occurs, and silver dichromate is obtained as a red solid. The overall chemical equation for the reaction is as follows:

$$2\,AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + 2\,KNO_3\,(aq)$$

What mass of $Ag_2Cr_2O_7$ is formed when 500 mL of 0.17 M $K_2Cr_2O_7$ are mixed with 250 mL of 0.57 M $AgNO_3$?

Given: balanced chemical equation and volume and concentration of each reactant

Asked for: mass of product

Strategy:

A. Calculate the number of moles of each reactant by multiplying the volume of each solution by its molarity.

B. Determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation.

C. Use mole ratios to calculate the number of moles of product that can be formed from the limiting reactant. Multiply the number of moles of the product by its molar mass to obtain the corresponding mass of product.

Solution:

A The balanced chemical equation tells us that 2 mol of $AgNO_3$(aq) reacts with 1 mol of $K_2Cr_2O_7$(aq) to form 1 mol of $Ag_2Cr_2O_7$(s) (Figure 8.3.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3$$

B Now determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$\mathrm{K_2Cr_2O_7}: \frac{0.085\ mol}{1\ mol} = 0.085$$

$$\mathrm{AgNO_3}: \frac{0.14\ mol}{2\ mol} = 0.070$$

Because 0.070 < 0.085, we know that $\mathrm{AgNO_3}$ is the *limiting reactant*.

C Each mole of $\mathrm{Ag_2Cr_2O_7}$ formed requires 2 mol of the limiting reactant ($\mathrm{AgNO_3}$), so we can obtain only 0.14/2 = 0.070 mol of $\mathrm{Ag_2Cr_2O_7}$. Finally, convert the number of moles of $\mathrm{Ag_2Cr_2O_7}$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7$$

The Ag^+ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $\mathrm{Ag_2Cr_2O_7}$, while the K^+ and NO_3^- ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

Exercise 8.5.3

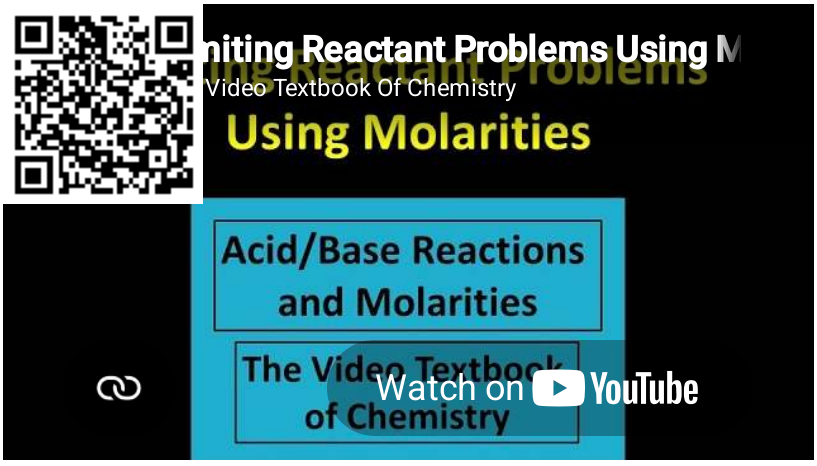
Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$2\,\mathrm{NaHCO_3\,(aq)} + \mathrm{H_2SO_4\,(aq)} \rightarrow 2\,\mathrm{CO_2\,(g)} + \mathrm{Na_2SO_4\,(aq)} + 2\,\mathrm{H_2O\,(l)}$$

If 13.0 mL of 3.0 M H_2SO_4 are added to 732 mL of 0.112 M $NaHCO_3$, what mass of CO_2 is produced?

Answer

3.4 g



Limiting Reactant Problems Using Molarities: Limiting Reactant Problems Using Molarities, YouTube(opens in new window) [youtu.be]eOXTliL-gNw (opens in new window)

Theoretical Yields

When reactants are not present in stoichiometric quantities, the limiting reactant determines the maximum amount of product that can be formed from the reactants. The amount of product calculated in this way is the theoretical yield, the amount obtained if the

reaction occurred perfectly and the purification method were 100% efficient.

In reality, less product is always obtained than is theoretically possible because of mechanical losses (such as spilling), separation procedures that are not 100% efficient, competing reactions that form undesired products, and reactions that simply do not run to completion, resulting in a mixture of products and reactants; this last possibility is a common occurrence. Therefore, the actual yield, the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

$$\text{percent yield} = \frac{\text{actual yield } (g)}{\text{theoretical yield } (g)} \times 100\% \tag{8.5.5}$$

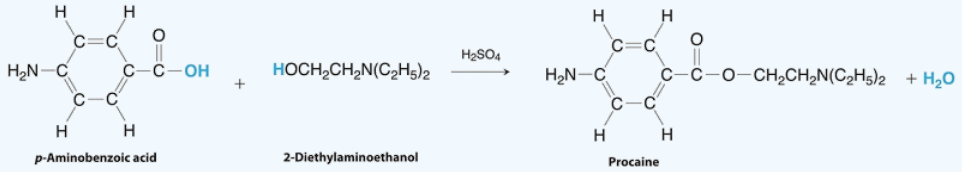
The method used to calculate the percent yield of a reaction is illustrated in Example 8.5.4.

Example 8.5.4: Novocain

Procaine is a key component of Novocain, an injectable local anesthetic used in dental work and minor surgery. Procaine can be prepared in the presence of H2SO4 (indicated above the arrow) by the reaction

$$\underset{\text{p-amino benzoic acid}}{C_7H_7NO_2} + \underset{\text{2-diethylaminoethanol}}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{\text{procaine}}{C_{13}H_{20}N_2O_2} + H_2O$$

If this reaction were carried out with 10.0 g of p-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and 15.7 g of procaine were isolated, what is the percent yield?



The preparation of procaine. A reaction of p-aminobenzoic acid with 2-diethylaminoethanol yields procaine and water.

Given: masses of reactants and product

Asked for: percent yield

Strategy:

A. Write the balanced chemical equation.
B. Convert from mass of reactants and product to moles using molar masses and then use mole ratios to determine which is the limiting reactant. Based on the number of moles of the limiting reactant, use mole ratios to determine the theoretical yield.
C. Calculate the percent yield by dividing the actual yield by the theoretical yield and multiplying by 100.

Solution:

A From the formulas given for the reactants and the products, we see that the chemical equation is balanced as written. According to the equation, 1 mol of each reactant combines to give 1 mol of product plus 1 mol of water.

B To determine which reactant is limiting, we need to know their molar masses, which are calculated from their structural formulas: p-aminobenzoic acid ($C_7H_7NO_2$), 137.14 g/mol; 2-diethylaminoethanol ($C_6H_{15}NO$), 117.19 g/mol. Thus the reaction used the following numbers of moles of reactants:

$$mol \text{ p-aminobenzoic acid} = 10.0\,g \times \frac{1\,mol}{137.14\,g} = 0.0729\,mol \text{ p-aminbenzoic acid}$$

$$mol \text{ 2-diethylaminoethanol} = 10.0\,g \times \frac{1\,mol}{117.19\,g} = 0.0853\,mol \text{ 2-diethylaminoethanol}$$

The reaction requires a 1:1 mole ratio of the two reactants, so p-aminobenzoic acid is the limiting reactant. Based on the coefficients in the balanced chemical equation, 1 mol of p-aminobenzoic acid yields 1 mol of procaine. We can therefore obtain

only a maximum of 0.0729 mol of procaine. To calculate the corresponding mass of procaine, we use its structural formula (C13H20N2O2) to calculate its molar mass, which is 236.31 g/mol.

$$\text{theoretical yield of procaine} = 0.0729\,mol \times \frac{236.31\,g}{1\,mol} = 17.2\,g$$

C The actual yield was only 15.7 g of procaine, so the percent yield (via Equation 8.5.5) is

$$\text{percent yield} = \frac{15.7\,g}{17.2\,g} \times 100 = 91.3\%$$

(If the product were pure and dry, this yield would indicate very good lab technique!)

? Exercise 8.5.4: Extraction of Lead

Lead was one of the earliest metals to be isolated in pure form. It occurs as concentrated deposits of a distinctive ore called galena (PbS), which is easily converted to lead oxide (PbO) in 100% yield by roasting in air via the following reaction:

$$2\,\mathrm{PbS\,(s)} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{PbO\,(s)} + 2\,\mathrm{SO_2\,(g)}$$

The resulting PbO is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:

$$\mathrm{PbO\,(s)} + \mathrm{C\,(s)} \rightarrow \mathrm{Pb\,(l)} + \mathrm{CO\,(g)}$$

If 93.3 kg of PbO is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?



Electrolytically refined pure (99.989 %) superficially oxidized lead nodules and a high purity (99.989 %) $1\ cm^3$ lead cube for comparison. Figure used with permission from Wikipedia.

Answer

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.

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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8.6: Three Examples of Chemical Reactions- Combustion, Alkali Metals, and Halogens



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CHAPTER OVERVIEW

9: Introduction to Solutions and Aqueous Reactions

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9.4: Types of Aqueous Solutions and Solubility
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9.1: Molecular Gastronomy



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9.2: Solution Concentration

Learning Objectives

- To describe the concentrations of solutions quantitatively

Many people have a qualitative idea of what is meant by *concentration*. Anyone who has made instant coffee or lemonade knows that too much powder gives a strongly flavored, highly concentrated drink, whereas too little results in a dilute solution that may be hard to distinguish from water. In chemistry, the concentration of a solution is the quantity of a **solute** that is contained in a particular quantity of **solvent** or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for solution reactions. Chemists use many different methods to define concentrations, some of which are described in this section.

Molarity

The most common unit of concentration is *molarity*, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The molarity (M) is defined as the number of moles of solute present in exactly 1 L of solution. It is, equivalently, the number of millimoles of solute present in exactly 1 mL of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{9.2.1}$$

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as M. An aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M. In chemical notation, square brackets around the name or formula of the solute represent the molar concentration of a solute. Therefore,

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

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

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{9.2.2}$$

or

$$V_{mL} M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles \tag{9.2.3}$$

Figure 9.2.1 illustrates the use of Equations 9.2.2 and 9.2.3.

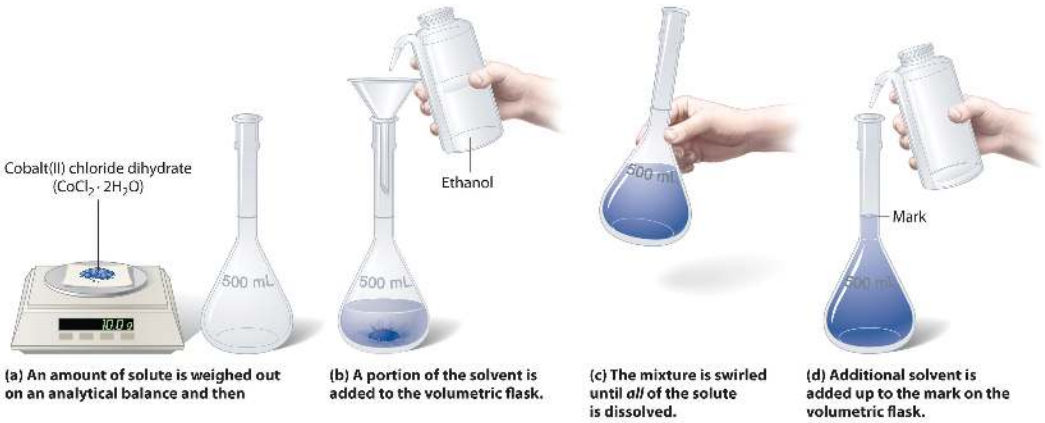


Figure 9.2.1: Preparation of a Solution of Known Concentration Using a Solid Solute

Example 9.2.1: Calculating Moles from Concentration of NaOH

Calculate the number of moles of sodium hydroxide (NaOH) in 2.50 L of 0.100 M NaOH.

Given: identity of solute and volume and molarity of solution

Asked for: amount of solute in moles

Strategy:

Use either Equation 9.2.2 or Equation 9.2.3, 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 9.2.2 is more useful:

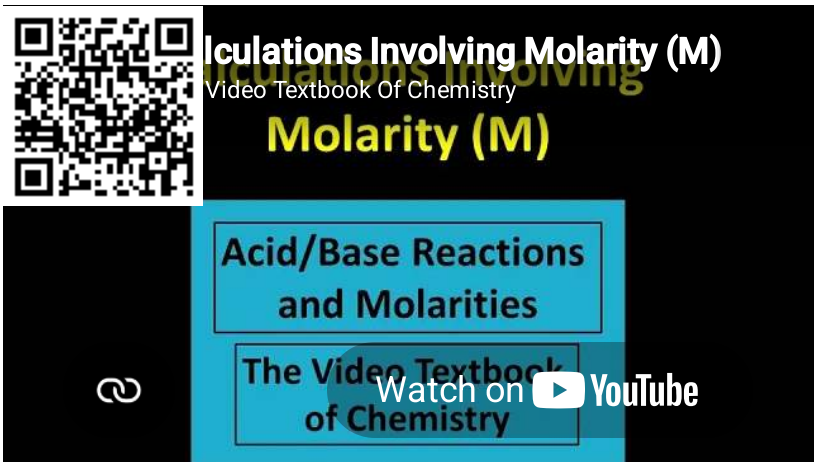
$$moles\ NaOH = V_L M_{mol/L} = (2.50\ \cancel{L}) \left(\frac{0.100\ mol}{\cancel{L}} \right) = 0.250\ mol\ NaOH$$

Exercise 9.2.1: Calculating Moles from Concentration of Alanine

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

Answer

41.6 mmol



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

Concentrations are also often reported on a mass-to-mass (m/m) basis or on a mass-to-volume (m/v) basis, particularly in clinical laboratories and engineering applications. A concentration expressed on an m/m basis is equal to the number of grams of solute per gram of solution; a concentration on an m/v basis is the number of grams of solute per milliliter of solution. Each measurement can be expressed as a percentage by multiplying the ratio by 100; the result is reported as percent m/m or percent m/v. The concentrations of very dilute solutions are often expressed in *parts per million* (*ppm*), which is grams of solute per 10^6 g of solution, or in *parts per billion* (*ppb*), which is grams of solute per 10^9 g of solution. For aqueous solutions at 20°C, 1 ppm corresponds to 1 µg per milliliter, and 1 ppb corresponds to 1 ng per milliliter. These concentrations and their units are summarized in Table 9.2.1.

Table 9.2.1: Common Units of Concentration

Concentration	Units
m/m	g of solute/g of solution
m/v	g of solute/mL of solution
ppm	g of solute/10^6 g of solution
	µg/mL
ppb	g of solute/10^9 g of solution
	ng/mL

The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution. Figure 9.2.1 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 9.2.2, for some substances this effect can be significant, especially for concentrated solutions.

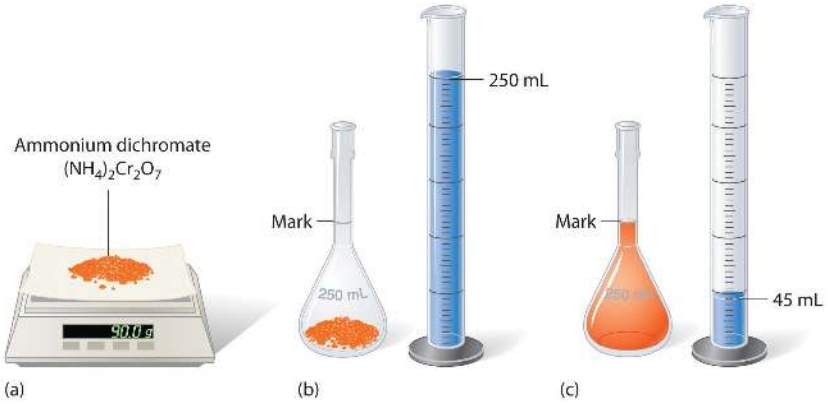


Figure 9.2.2: Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

Example 9.2.2

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

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $CoCl_2 \cdot 2\,H_2O$, divide the mass of the compound by its molar mass. Calculate the molarity of the solution by dividing the number of moles of solute by the volume of the solution in liters.

Solution:

The molar mass of $CoCl_2$•$2H_2O$ is 165.87 g/mol. Therefore,

$$moles\ CoCl_2 \cdot 2H_2O = \left(\frac{10.0\ \cancel{g}}{165.87\ \cancel{g}/mol}\right) = 0.0603\ mol$$

The volume of the solution in liters is

$$volume = 500 \cancel{mL}\left(\frac{1\ L}{1000\ \cancel{mL}}\right) = 0.500\ L$$

Molarity is the number of moles of solute per liter of solution, so the molarity of the solution is

$$molarity = \frac{0.0603\ mol}{0.500\ L} = 0.121\ M = CoCl_2 \cdot H_2O$$

Exercise 9.2.2

The solution shown in Figure 9.2.2 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 9.2.2. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 9.2.3.

Example 9.2.3: D5W Solution

The so-called D5W solution used for the intravenous replacement of body fluids contains 0.310 M glucose. (D5W is an approximately 5% solution of dextrose [the medical name for glucose] in water.) Calculate the mass of glucose necessary to prepare a 500 mL pouch of D5W. Glucose has a molar mass of 180.16 g/mol.

Given: molarity, volume, and molar mass of solute

Asked for: mass of solute

Strategy:

A. Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.

B. Obtain the mass of glucose needed by multiplying the number of moles of the compound by its molar mass.

Solution:

A We must first calculate the number of moles of glucose contained in 500 mL of a 0.310 M solution:

$$V_L M_{mol/L} = moles$$

$$500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) = 0.155\ mol\ glucose$$

B We then convert the number of moles of glucose to the required mass of glucose:

$$mass\ of\ glucose = 0.155\ \cancel{mol\ glucose}\left(\frac{180.16\ g\ glucose}{1\ \cancel{mol\ glucose}}\right) = 27.9\ g\ glucose$$

Exercise 9.2.3

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 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 9.2.3. It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute. Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{9.2.4}$$

where the subscripts *s* and *d* indicate the stock and dilute solutions, respectively. Example 9.2.4 demonstrates the calculations involved in diluting a concentrated stock solution.



Figure 9.2.3: 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 9.2.4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 9.2.3?

Given: volume and molarity of dilute solution

Asked for: volume of stock solution

Strategy:

A. Calculate the number of moles of glucose contained in the indicated volume of dilute solution by multiplying the volume of the solution by its molarity.

B. To determine the volume of stock solution needed, divide the number of moles of glucose by the molarity of the stock solution.

Solution:

A The D5W solution in Example 4.5.3 was 0.310 M glucose. We begin by using Equation 4.5.4 to calculate the number of moles of glucose contained in 2500 mL of the solution:

$$moles\ glucose = 2500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) = 0.775\ mol\ glucose$$

B We must now determine the volume of the 3.00 M stock solution that contains this amount of glucose:

$$volume\ of\ stock\ soln = 0.775\ \cancel{mol\ glucose}\left(\frac{1\ L}{3.00\ \cancel{mol\ glucose}}\right) = 0.258\ L\ or\ 258\ mL$$

In determining the volume of stock solution that was needed, we had to divide the desired number of moles of glucose by the concentration of the stock solution to obtain the appropriate units. Also, the number of moles of solute in 258 mL of the stock solution is the same as the number of moles in 2500 mL of the more dilute solution; *only the amount of solvent has changed*. The answer we obtained makes sense: diluting the stock solution about tenfold increases its volume by about a factor of 10 (258 mL → 2500 mL). Consequently, the concentration of the solute must decrease by about a factor of 10, as it does (3.00 M → 0.310 M).

We could also have solved this problem in a single step by solving Equation 4.5.4 for V_s and substituting the appropriate values:

$$V_s = \frac{(V_d)(M_d)}{M_s} = \frac{(2.500\ L)(0.310\ \cancel{M})}{3.00\ \cancel{M}} = 0.258\ L$$

As we have noted, there is often more than one correct way to solve a problem.

Exercise 9.2.4

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

Example 9.2.5

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

a. 0.21 M NaOH
b. 3.7 M $(CH_3)_2CHOH$
c. 0.032 M $In(NO_3)_3$

Given: molarity

Asked for: concentrations

Strategy:

A Classify each compound as either a strong electrolyte or a nonelectrolyte.

B If the compound is a nonelectrolyte, its concentration is the same as the molarity of the solution. If the compound is a strong electrolyte, determine the number of each ion contained in one formula unit. Find the concentration of each species by multiplying the number of each ion by the molarity of the solution.

Solution:

1. Sodium hydroxide is an ionic compound that is a strong electrolyte (and a strong base) in aqueous solution:
   $NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$

   B Because each formula unit of NaOH produces one Na^+ ion and one OH^- ion, the concentration of each ion is the same as the concentration of NaOH: $[Na^+]$ = 0.21 M and $[OH^-]$ = 0.21 M.

2. **A** The formula $(CH_3)_2CHOH$ represents 2-propanol (isopropyl alcohol) and contains the –OH group, so it is an alcohol. Recall from Section 4.1 that alcohols are covalent compounds that dissolve in water to give solutions of neutral molecules. Thus alcohols are nonelectrolytes.

   B The only solute species in solution is therefore $(CH_3)_2CHOH$ molecules, so $[(CH_3)_2CHOH] = 3.7$ M.

3. **A** Indium nitrate is an ionic compound that contains In^{3+} ions and NO_3^- ions, so we expect it to behave like a strong electrolyte in aqueous solution:

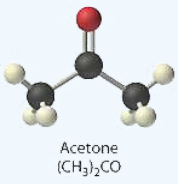
$$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

   B One formula unit of $In(NO_3)_3$ produces one In^{3+} ion and three NO_3^- ions, so a 0.032 M $In(NO_3)_3$ solution contains 0.032 M In^{3+} and 3 × 0.032 M = 0.096 M NO_3^-—that is, $[In^{3+}] = 0.032$ M and $[NO_3^-] = 0.096$ M.

? Exercise 9.2.5

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

a. 0.0012 M $Ba(OH)_2$
b. 0.17 M Na_2SO_4
c. 0.50 M $(CH_3)_2CO$, commonly known as acetone



Answer a

$[Ba^{2+}] = 0.0012\ M;\ [OH^-] = 0.0024\ M$

Answer b

$[Na^+] = 0.34\ M;\ [SO_4^{2-}] = 0.17\ M$

Answer c

$[(CH_3)_2CO] = 0.50\ M$

Summary

Solution concentrations are typically expressed as molarities and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.

- **definition of molarity:**

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

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

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

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

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

The **concentration** of a substance is the quantity of solute present in a given quantity of solution. Concentrations are usually expressed in terms of **molarity**, defined as the number of moles of solute in 1 L of solution. Solutions of known concentration can

be prepared either by dissolving a known mass of solute in a solvent and diluting to a desired final volume or by diluting the appropriate volume of a more concentrated solution (a **stock solution**) to the desired final volume.

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9.3: Solution Stoichiomentry

Learning Objectives

- How to calculate the concentrations of ions when a salt is dissolved

In Example 9.3.2, 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:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \tag{9.3.1}$$

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 9.3.4).

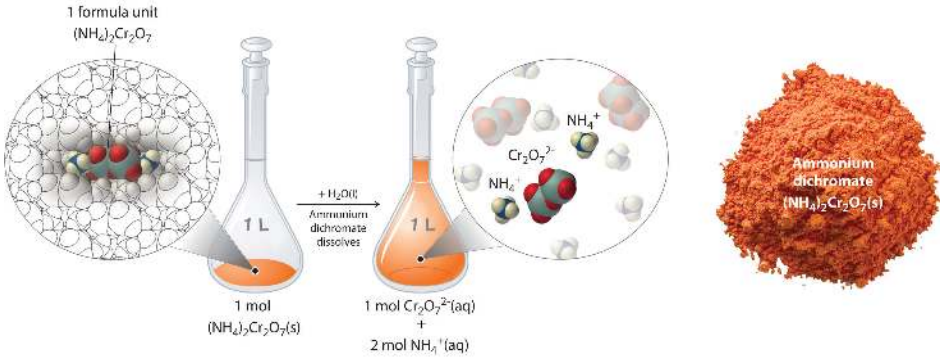
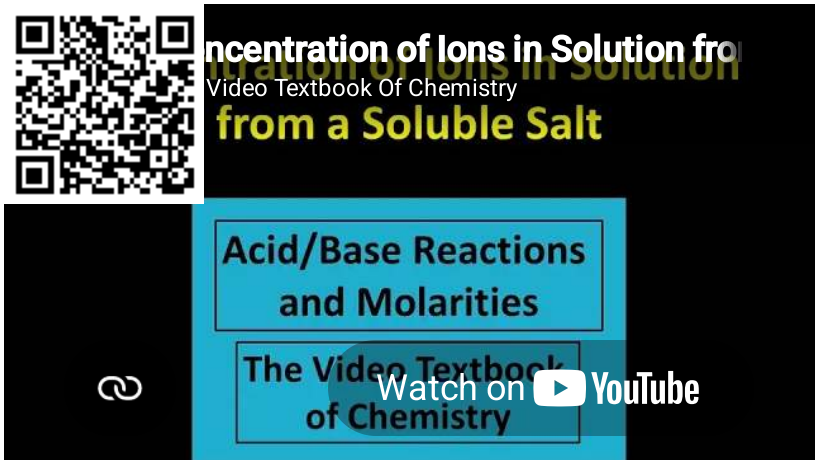


Figure 9.3.4: Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

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.



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

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9.4: Types of Aqueous Solutions and Solubility

8.9A: Electrolytes and Electrolytic Solutions

8.9B: The nature of ions in aqueous solution

https://chem.libretexts.org/Textbook...A_Electrolytes

In Binary Ionic Compounds and Their Properties we point out that when an ionic compound dissolves in water, the positive and negative ions originally present in the crystal lattice persist in solution. Their ability to move nearly independently through the solution permits them to carry positive or negative electrical charges from one place to another. Hence the solution conducts an electrical current.

Electrolytes

Substances whose solutions conduct electricity are called electrolytes. All soluble ionic compounds are strong electrolytes. They conduct very well because they provide a plentiful supply of ions in solution. Some polar covalent compounds are also strong electrolytes. Common examples are HCl, HBr, HI and H_2SO_4, all of which react with H_2O to form large concentrations of ions. A solution of HCl, for example, conducts even better than one of NaCl having the same concentration.

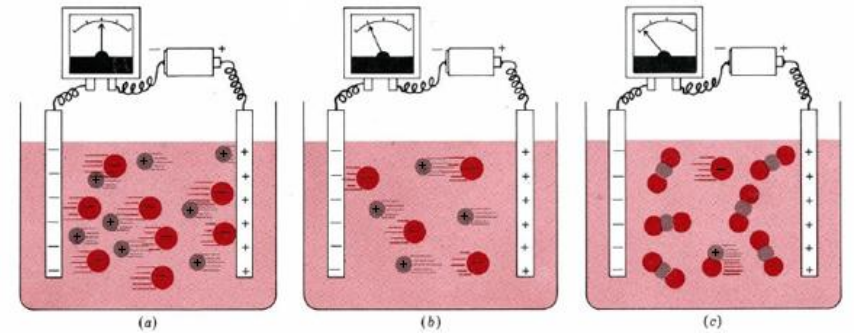


Figure 9.4.1: The conductivity of electrolyte solutions: (a) 0.1 M NaCl (b) 0.05 M NaCl (c) 0.1 M $HgCl_2$. An electrolyte solution conducts electricity because of the movement of ions in the solution (see above). The larger the concentration of ions, the better the solutions conducts. Weak electrolytes, such as $HgCl_2$, conduct badly because they produce few ions when dissolved (low concentration of ions) and exist mainly in the form of molecules.

The effect of the concentration of ions on the electrical current flowing through a solution is illustrated in Figure 9.4.1. Part *a* of the figure shows what happens when a battery is connected through an electrical meter to two inert metal strips (**electrodes**) dipping in ethanol. Each cubic decimeter of such a solution contains 0.10 mol NaCl (that is, 0.10 mol Na^+ and 0.10 mol Cl^-). An electrical current is carried through the solution both by the Na^+ ions moving toward the negative electrode and by the Cl^- ions which are attracted toward the positive electrode. The dial on the meter indicates the quantity of current.

Figure 1*b* shows that if we replace the 0.10-*M* NaCl solution with a 0.05-*M* NaCl solution, the meter reading falls to about one-half its former value. Halving the concentration of NaCl halves the number of ions between the electrodes, and half as many ions can only carry half as much electrical charge. Therefore the current is half as great. Because it responds in such a direct way to the concentration of ions, conductivity of electrical current is a useful tool in the study of solutions.

Conductivity measurements reveal that most covalent compounds, if they dissolve in water at all, retain their original molecular structures. Neutral molecules cannot carry electrical charges through the solution, and so no current flows. A substance whose aqueous solution conducts no better than water itself is called a **nonelectrolyte**. Some examples are oxygen, O_2, ethanol, C_2H_5OH, and sugar, $C_{12}H_{22}O_{11}$.

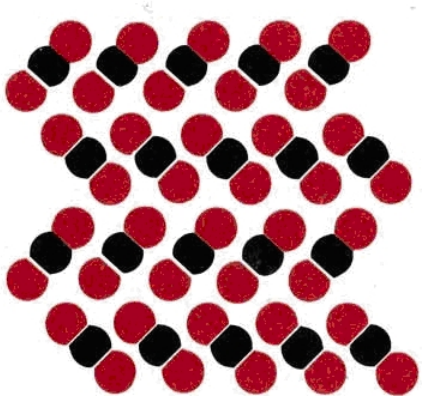


Figure 9.4.2: Mercury Bromide Crystals.

Some covalent substances behave as **weak electrolytes**—their solutions allow only a small current flow, but it is greater than that of the pure solvent. An example is mercury(II) chloride (seen in the Figure above). For a 100-*M* $HgCl_2$ solution the meter reading shows only about 0.2 percent as much current as for 0.10 *M* NaCl. A crystal of $HgCl_2$ consists of discrete molecules, like those shown for $HgBr_2$ in Figure 9.4.2. When the solid dissolves, most of these molecules remain intact, but a few dissociate into ions according to the equation

$$\underbrace{HgCl_2}_{99.8\%} \rightleftharpoons \underbrace{HgCl^+}_{0.2\%} + Cl^-$$

(The double arrows indicate that the ionization proceeds only to a limited extent and an equilibrium state is attained.) Since only 0.2 percent of the $HgCl_2$ forms ions, the 0.10 *M* solution can conduct only about 0.2 percent as much current as 0.10 *M* NaCl.

Conductivity measurements can tell us more than whether a substance is a strong, a weak, or a nonelectrolyte. Consider, for instance, the data in Table 9.4.1 which shows the electrical current conducted through various aqueous solutions under identical conditions. At the rather low concentration of 0.001 *M*, the strong electrolyte solutions conduct between 2500 and 10 000 times as much current as pure H_2O and about 10 times as much as the weak electrolytes $HC_2H_3O_2$ (acetic acid) and NH_3 (ammonia).

Closer examination of the data for strong electrolytes reveals that some compounds which contain H or OH groups [such as HCl or $Ba(OH)_2$] conduct unusually well. If these compounds are excluded, we find that 1:1 electrolytes (compounds which consist of equal numbers of +1 ions and –1 ions) usually conduct about half as much current as 2:2 electrolytes (+2 and -2 ions), 1:2 electrolytes (+1 and -2 ions), or 2:1 electrolytes (+2 and -1 ions).

TABLE 9.4.1: Electrical Current Conducted Through Various 0.001 M Aqueous Solutions at 18°C.*

Substance	*Current /mA*	Substance	*Current /mA*
Pure Water		**1:2 Electrolytes**	
H_2O	3.69 x 10^{-4}	Na_2SO_4	2.134
Weak Electrolytes		Na_2CO_3	2.24
$HC_2H_3O_2$	0.41	K_2CO_3	2.660
NH_3	0.28	**2:1 Electrolytes**	
1:1 Electrolytes		$MgCl_2$	2.128
NaCl	1.065	$CaCl_2$	2.239
NaI	1.069	$SrCl_2$	2.290
KCl	1.273	$BaCl_2$	2.312
KI	1,282	$Ba(OH)_2$	4.14
$AgNO_3$	1.131	**2:2 Electrolytes**	
HCl	3.77	$MgSO_4$	2.00
HNO_3	3.75	$CaSO_4$	2.086
NaOH	2.08	$CuSO_4$	1.97
KOH	2.34	$ZnSO_4$	1.97

* All measurements refer to a cell in which the distance between the electrodes is 1.0 mm and the area of each electrode is 1.0 cm². A potential difference of 1.0 V is applied to produce the tabulated currents.

There is a simple reason for this behavior. Under similar conditions, most ions move through water at comparable speeds. This means that ions like Mg^{2+} or SO_4^{2-}, which are doubly charged, will carry twice as much current through the solution as will singly charged ions like Na^+ or Cl^-. Consequently, a 0.001 *M* solution of a 2:2 electrolyte like $MgSO_4$ will conduct about twice as well as a 0.001 M solution of a 1:1 electrolyte like NaCl.

A similar argument applies to solutions of 1:2 and 2:1 electrolytes. A solution like 0.001 *M* Na_2SO_4 conducts about twice as well as 0.001 *M* NaCl partly because there are twice as many Na^- ions available to move when a battery is connected, but also because SO_4^{2-} ions carry twice as much charge as Cl^- ions when moving at the same speed. These differences in conductivity between different types of strong electrolytes can sometimes be very useful in deciding what ions are actually present in a given electrolyte solution as the following example makes clear.

A second, slightly more subtle, conclusion can be drawn from the data in Table 9.4.1. When an electrolyte dissolves, each type of ion makes an independent contribution to the current the solution conducts. This can be seen by comparing NaCl with KCl, and NaI with KI. In each case the compound containing K^+ conducts about 0.2 mA more than the one containing Na^+. If we apply this observation to Na_2CO_3 and K_2CO_3, each of which produces twice as many Na^+ or K^+ ions in solution, we find that the difference in current is also twice as great—about 0.4 mA.

Thus conductivity measurements confirm our statement that each ion exhibits its own characteristic properties in aqueous solutions, independent of the presence of other ions. One such characteristic property is the quantity of electrical current that a given concentration of a certain type of ion can carry.

✔ Example 9.4.1: Ions

At 18°C a 0.001-*M* aqueous solution of potassium hydrogen carbonate, $KHCO_3$, conducts a current of 1.10 mA in a cell of the same design as that used to obtain the data in Table 11.1. What ions are present in solution?

Solution

Referring to Table 6.2 which lists possible polyatomic ions, we can arrive at three possibilities for the ions from which $KHCO_3$ is made:

a. K^+ and H^+ and C^{4+} and three O^{2-}
b. K^+ and H^+ and CO_3^{2-}
c. K^+ and HCO_3^-

Since the current conducted by the solution falls in the range of 1.0 to 1.3 mA characteristic of 1:1 electrolytes, possibility *c* is the only reasonable choice.

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9.5: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubilities.

Exchange (Double-Displacement) Reactions

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. We described a precipitation reaction in which a colorless solution of silver nitrate was mixed with a yellow-orange solution of potassium dichromate to give a reddish precipitate of silver dichromate:

$$\mathrm{AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + KNO_3\,(aq)} \tag{9.5.1}$$

This unbalanced equation has the general form of an exchange reaction:

$$\overbrace{\mathrm{AC}}^{\text{soluble}} + \overbrace{\mathrm{BD}}^{\text{soluble}} \rightarrow \underbrace{\mathrm{AD}}_{\text{insoluble}} + \overbrace{\mathrm{BC}}^{\text{soluble}} \tag{9.5.2}$$

The solubility and insoluble annotations are specific to the reaction in Equation 9.5.1 and not characteristic of all exchange reactions (e.g., both products can be soluble or insoluble). *Precipitation reactions* are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called *double-displacement reactions*. Two important uses of precipitation reactions are to isolate metals that have been extracted from their ores and to recover precious metals for recycling.



Video 9.5.1***:*** *Mixing Potassium Chromate and Silver Nitrate together to initiate a precipitation reaction (Equation 9.5.1).*

While full chemical equations show the identities of the reactants and the products and give the stoichiometries of the reactions, they are less effective at describing what is actually occurring in solution. In contrast, equations that show only the hydrated species focus our attention on the chemistry that is taking place and allow us to see similarities between reactions that might not otherwise be apparent.

Let's consider the reaction of silver nitrate with potassium dichromate above. When aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall balanced chemical equation for the reaction shows each reactant and product as undissociated, electrically neutral compounds:

$$\mathrm{2\,AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + 2\,KNO_3\,(aq)} \tag{9.5.3}$$

Although Equation 9.5.3 gives the identity of the reactants and the products, it does not show the identities of the actual species in solution. Because ionic substances such as $\mathrm{AgNO_3}$ and $\mathrm{K_2Cr_2O_7}$ are *strong electrolytes* (i.e., they dissociate completely in aqueous solution to form ions). In contrast, because $\mathrm{Ag_2Cr_2O_7}$ is not very soluble, it separates from the solution as a solid. To find out what

is actually occurring in solution, it is more informative to write the reaction as a complete ionic equation showing which ions and molecules are hydrated and which are present in other forms and phases:

$$\begin{aligned} 2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{NO_3^-(aq)} + 2\,\mathrm{K^+(aq)} + \mathrm{Cr_2O_7^{2-}(aq)} \;&\rightarrow \mathrm{Ag_2Cr_2O_7(s)} \\ + 2\,\mathrm{K^+(aq)} + 2\,\mathrm{NO_3^-(aq)} & \end{aligned} \tag{9.5.4}$$

Note that $\mathrm{K^+(aq)}$ and $\mathrm{NO_3^-(aq)}$ ions are present on both sides of Equation 9.5.4 and their coefficients are the same on both sides. These ions are called *spectator ions* because they do not participate in the actual reaction. Canceling the spectator ions gives the net ionic equation, which shows only those species that participate in the chemical reaction:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{9.5.5}$$

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 9.5.5, the charge on the left side is 2(+1) + 1(−2) = 0, which is the same as the charge of a neutral $\mathrm{Ag_2Cr_2O_7}$ formula unit on the right side.

By eliminating the spectator ions, we can focus on the chemistry that takes place in a solution. For example, the overall chemical equation for the reaction between silver fluoride and ammonium dichromate is as follows:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \tag{9.5.6}$$

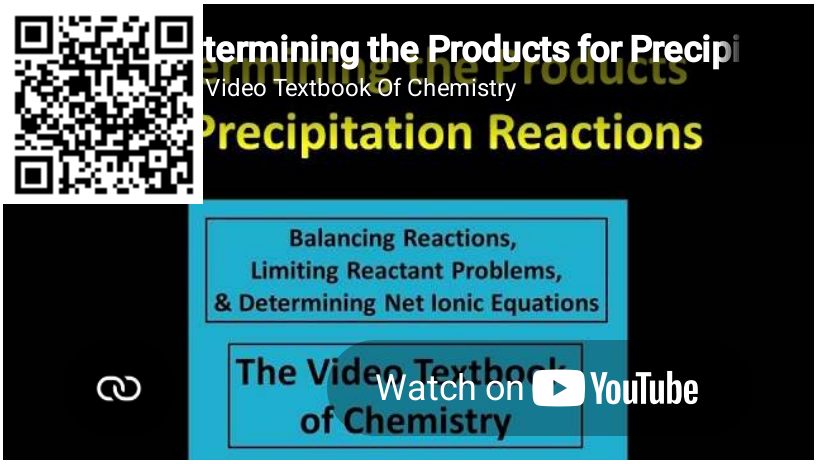
The complete ionic equation for this reaction is as follows:

$$\begin{aligned} 2\,\mathrm{Ag^+(aq)} + \cancel{2\,\mathrm{F^-(aq)}} + \cancel{2\,\mathrm{NH_4^+(aq)}} + \mathrm{Cr_2O_7^{2-}(aq)} \\ \rightarrow \mathrm{Ag_2Cr_2O_7(s)} + \cancel{2\,\mathrm{NH_4^+(aq)}} + \cancel{2\,\mathrm{F^-(aq)}} \end{aligned} \tag{9.5.7}$$

Because two $\mathrm{NH_4^+(aq)}$ and two $\mathrm{F^-(aq)}$ ions appear on both sides of Equation 9.5.7, they are spectator ions. They can therefore be canceled to give the **net ionic equation** (Equation 9.5.8), which is identical to Equation 9.5.5:

$$2\,\mathrm{Ag^+(aq)} + \mathrm{Cr_2O_7^{2-}(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} \tag{9.5.8}$$

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.



Determining the Products for Precipitation Reactions: Determining the Products for Precipitation Reactions, YouTube(opens in new window) [youtu.be]

Example 9.5.1: Balancing Precipitation Equations

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous barium nitrate with aqueous sodium phosphate to give solid barium phosphate and a solution of sodium nitrate.

Given: reactants and products

Asked for: overall, complete ionic, and net ionic equations

Strategy:

Write and balance the overall chemical equation. Write all the soluble reactants and products in their dissociated form to give the complete ionic equation; then cancel species that appear on both sides of the complete ionic equation to give the net ionic equation.

Solution:

From the information given, we can write the unbalanced chemical equation for the reaction:

$$\mathrm{Ba(NO_3)_2\,(aq) + Na_3PO_4\,(aq) \rightarrow Ba_3(PO_4)_2\,(s) + NaNO_3\,(aq)}$$

Because the product is $Ba_3(PO_4)_2$, which contains three Ba^{2+} ions and two PO_4^{3-} ions per formula unit, we can balance the equation by inspection:

$$\mathrm{3\,Ba(NO_3)_2\,(aq) + 2\,Na_3PO_4\,(aq) \rightarrow Ba_3(PO_4)_2\,(s) + 6\,NaNO_3\,(aq)}$$

This is the overall balanced chemical equation for the reaction, showing the reactants and products in their undissociated form. To obtain the complete ionic equation, we write each soluble reactant and product in dissociated form:

$$\mathrm{3\,Ba^{2+}\,(aq) + \cancel{6\,NO_3^-\,(aq)} + \cancel{6\,Na^+\,(aq)} + 2\,PO_4^{3-}\,(aq) \rightarrow Ba_3(PO_4)_2\,(s) + \cancel{6\,Na^+\,(aq)} + \cancel{6\,NO_3^-\,(aq)}}$$

The six $NO_3^-(aq)$ ions and the six $Na^+(aq)$ ions that appear on both sides of the equation are spectator ions that can be canceled to give the net ionic equation:

$$\mathrm{3\,Ba^{2+}\,(aq) + 2\,PO_4^{3-}\,(aq) \rightarrow Ba_3(PO_4)_2\,(s)}$$

? Exercise 9.5.1: 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:

$$\mathrm{3\,AgF\,(aq) + Na_3PO_4\,(aq) \rightarrow Ag_3PO_4\,(s) + 3\,NaF\,(aq)}$$

complete ionic equation:

$$\mathrm{3\,Ag^+\,(aq) + 3\,F^-\,(aq) + 3\,Na^+\,(aq) + PO_4^{3-}\,(aq) \rightarrow Ag_3PO_4\,(s) + 3\,Na^+\,(aq) + 3\,F^-\,(aq)}$$

net ionic equation:

$$\mathrm{3\,Ag^+\,(aq) + PO_4^{3-}\,(aq) \rightarrow Ag_3PO_4\,(s)}$$

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.

Predicting Solubilities

Table 9.5.1 gives guidelines for predicting the solubility of a wide variety of ionic compounds. To determine whether a precipitation reaction will occur, we identify each species in the solution and then refer to Table 9.5.1 to see which, if any, combination(s) of cation and anion are likely to produce an insoluble salt. In doing so, it is important to recognize that *soluble* and *insoluble* are relative terms that span a wide range of actual solubilities. We will discuss solubilities in more detail later, where you will learn that very small amounts of the constituent ions remain in solution even after precipitation of an "insoluble" salt. For our purposes, however, we will assume that precipitation of an insoluble salt is complete.

Table 9.5.1: Guidelines for Predicting the Solubility of Ionic Compounds in Water

Soluble			**Exceptions**
Rule 1	most salts that contain an alkali metal (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium (NH_4^+)		
Rule 2	most salts that contain the nitrate (NO_3^-) anion		
Rule 3	most salts of anions derived from monocarboxylic acids (e.g., $CH_3CO_2^-$)	but not	silver acetate and salts of long-chain carboxylates
Rule 4	most chloride, bromide, and iodide salts	but not	salts of metal ions located on the lower right side of the periodic table (e.g., Cu^+, Ag^+, Pb^{2+}, and Hg_2^{2+}).
	Insoluble		**Exceptions**
Rule 5	most salts that contain the hydroxide (OH^-) and sulfide (S^{2-}) anions	but not	salts of the alkali metals (group 1), the heavier alkaline earths (Ca^{2+}, Sr^{2+}, and Ba^{2+} in group 2), and the NH_4^+ ion.
Rule 6	most carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) salts	but not	salts of the alkali metals or the NH_4^+ ion.
Rule 7	most sulfate (SO_4^{2-}) salts that contain main group cations with a charge ≥ +2	but not	salts of +1 cations, Mg^{2+}, and dipositive transition metal cations (e.g., Ni^{2+})

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of a 1.0 M aqueous NaCl solution is mixed with 500 mL of a 1.0 M aqueous KBr solution, the final solution has a volume of 1.00 L and contains 0.50 M Na^+(aq), 0.50 M Cl^-(aq), 0.50 M K^+(aq), and 0.50 M Br^-(aq). As you will see in the following sections, none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other (Figure 9.5.1).

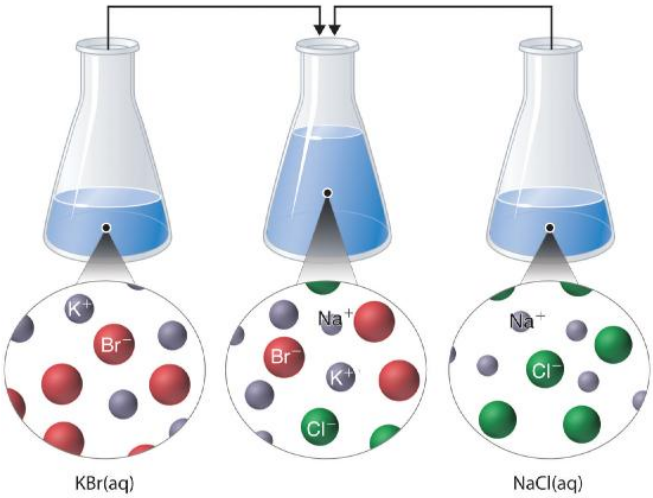


Figure 9.5.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

Example 9.5.2

Using the information in Table 9.5.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

a. Aqueous solutions of barium chloride and lithium sulfate are mixed.
b. Aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.
c. Aqueous solutions of strontium bromide and aluminum nitrate are mixed.
d. Solid lead(II) acetate is added to an aqueous solution of ammonium iodide.

Given: reactants

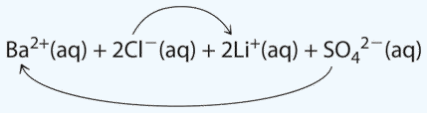
Asked for: reaction and net ionic equation

Strategy:

A. Identify the ions present in solution and write the products of each possible exchange reaction.
B. Refer to Table 9.5.1 to determine which, if any, of the products is insoluble and will therefore form a precipitate. If a precipitate forms, write the net ionic equation for the reaction.

Solution:

A Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains Ba^{2+}, Cl^-, Li^+, and SO_4^{2-} ions. The only possible exchange reaction is to form LiCl and $BaSO_4$:



B We now need to decide whether either of these products is insoluble. Table 9.5.1 shows that LiCl is soluble in water (rules 1 and 4), but $BaSO_4$ is not soluble in water (rule 5). Thus $BaSO_4$ will precipitate according to the net ionic equation

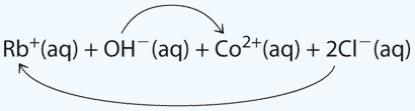
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

Although soluble barium salts are toxic, $BaSO_4$ is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a "barium milkshake" or a "barium enema"—a suspension of very fine $BaSO_4$ particles in water.



An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.” A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. from Wikipedia.

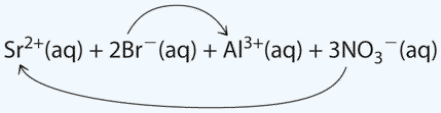
1. **A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains Rb^+, OH^-, Co^{2+}, and Cl^- ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide):



B According to Table 9.5.1, RbCl is soluble (rules 1 and 4), but $Co(OH)_2$ is not soluble (rule 5). Hence $Co(OH)_2$ will precipitate according to the following net ionic equation:

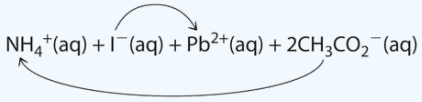
$$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$$

2. **A** When aqueous solutions of strontium bromide and aluminum nitrate are mixed, we initially obtain a solution that contains Sr^{2+}, Br^-, Al^{3+}, and NO_3^- ions. The two possible products from an exchange reaction are aluminum bromide and strontium nitrate:



B According to Table 9.5.1, both $AlBr_3$ (rule 4) and $Sr(NO_3)_2$ (rule 2) are soluble. Thus no net reaction will occur.

1. **A** According to Table 9.5.1, lead acetate is soluble (rule 3). Thus solid lead acetate dissolves in water to give Pb^{2+} and $CH_3CO_2^-$ ions. Because the solution also contains NH_4^+ and I^- ions, the possible products of an exchange reaction are ammonium acetate and lead(II) iodide:



B According to Table 9.5.1, ammonium acetate is soluble (rules 1 and 3), but PbI_2 is insoluble (rule 4). Thus $Pb(C_2H_3O_2)_2$ will dissolve, and PbI_2 will precipitate. The net ionic equation is as follows:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

? Exercise 9.5.2

Using the information in Table 9.5.1, predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

a. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
b. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
c. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer a

$Fe^{2+}(aq) + 2OH^{-}(aq) \rightarrow Fe(OH)_2(s)$

Answer b

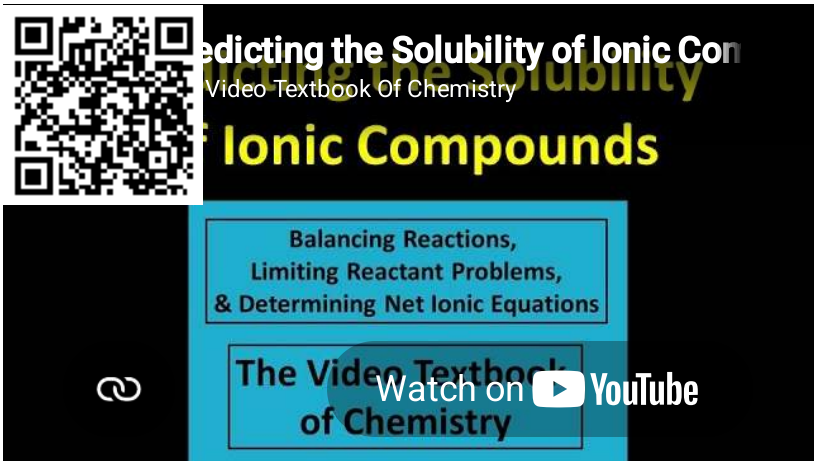
$2PO_4^{3-}(aq) + 3Hg^{2+}(aq) \rightarrow Hg_3(PO_4)_2(s)$

Answer c

$NaF(s)$ dissolves; no net reaction

Answer d

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$



Predicting the Solubility of Ionic Compounds: Predicting the Solubility of Ionic Compounds, YouTube(opens in new window) [youtu.be] (opens in new window)

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9.6: Representing Aqueous Reactions- Molecular, Ionic, and Complete Ionic Equations

Learning Objectives

- To understand what information is obtained by each type of ionic equation

The chemical equations discussed in Chapter 7 showed 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. As you learned in Example 9, when aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall chemical equationA chemical equation that shows all the reactants and products as undissociated, electrically neutral compounds. for the reaction shows each reactant and product as undissociated, electrically neutral compounds:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq) \tag{9.6.1}$$

Although Equation 9.6.1 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:

$$\begin{aligned} &2Ag^+(aq) + 2NO_3^-(aq) + 2K^+(aq) + Cr_2O_7^{2-}(aq) \\ &\rightarrow Ag_2Cr_2O_7(s) + 2K^+(aq) + 2NO_3^-(aq) \end{aligned} \tag{9.6.2}$$

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:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{9.6.3}$$

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 9.6.3, 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:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \tag{9.6.4}$$

The complete ionic equation for this reaction is as follows:

$$\begin{aligned} &2Ag^+(aq) + 2F^-(aq) + 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \\ &\rightarrow Ag_2Cr_2O_7(s) + 2NH_4^+(aq) + 2F^-(aq) \end{aligned} \tag{9.6.5}$$

Because two NH_4^+(aq) and two F^-(aq) ions appear on both sides of Equation 9.6.5, they are spectator ions. They can therefore be canceled to give the net ionic equation (Equation 9.6.6), which is identical to Equation 9.6.3:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{9.6.6}$$

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 9.6.1

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:

$$Ba(NO_3)_2(aq) + Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + NaNO_3(aq) \tag{9.6.7}$$

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:

$$3Ba(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6NaNO_3(aq) \tag{9.6.8}$$

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:

$$\begin{aligned} &3Ba^{2+}(aq) + 6NO_3^-(aq) + 6Na^+(aq) + 2PO_4^{3-}(aq) \\ &\rightarrow Ba_3(PO_4)_2(s) + 6Na^+(aq) + 6NO_3^-(aq) \end{aligned} \tag{9.6.9}$$

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:

$$3Ba^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s) \tag{9.6.10}$$

Exercise 9.6.1

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:

$$3AgF(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + 3NaF(aq) \tag{9.6.11}$$

complete ionic equation:

$$\begin{aligned} &3Ag^+(aq) + 3F^-(aq) + 3Na^+(aq) + PO_4^{3-}(aq) \\ &\rightarrow Ag_3PO_4(s) + 3Na^+(aq) + 3F^-(aq) \end{aligned} \tag{9.6.12}$$

net ionic equation:

$$3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) \tag{9.6.13}$$

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 introduced in Chapter 3 (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.

Summary

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.

Key Takeaway

- A complete ionic equation consists of the net ionic equation and spectator ions.

Conceptual Problem

1. What information can be obtained from a complete ionic equation that cannot be obtained from the overall chemical equation?

Contributors

- Modified by Joshua Halpern (Howard University)

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9.7: Acid-Base

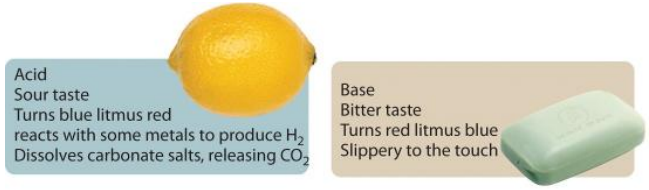
Learning Objectives

- To know the characteristic properties of acids and bases.

Acid–base reactions are essential in both biochemistry and industrial chemistry. Moreover, many of the substances we encounter in our homes, the supermarket, and the pharmacy are acids or bases. For example, aspirin is an acid (acetylsalicylic acid), and antacids are bases. In fact, every amateur chef who has prepared mayonnaise or squeezed a wedge of lemon to marinate a piece of fish has carried out an acid–base reaction. Before we discuss the characteristics of such reactions, let's first describe some of the properties of acids and bases.

Definitions of Acids and Bases

We can define **acids** as substances that dissolve in water to produce H^+ ions, whereas **bases** are defined as substances that dissolve in water to produce OH^- ions. In fact, this is only one possible set of definitions. Although the general properties of acids and bases have been known for more than a thousand years, the definitions of *acid* and *base* have changed dramatically as scientists have learned more about them. In ancient times, an acid was any substance that had a sour taste (e.g., vinegar or lemon juice), caused consistent color changes in dyes derived from plants (e.g., turning blue litmus paper red), reacted with certain metals to produce hydrogen gas and a solution of a salt containing a metal cation, and dissolved carbonate salts such as limestone ($CaCO_3$) with the evolution of carbon dioxide. In contrast, a base was any substance that had a bitter taste, felt slippery to the touch, and caused color changes in plant dyes that differed diametrically from the changes caused by acids (e.g., turning red litmus paper blue). Although these definitions were useful, they were entirely descriptive.



The Arrhenius Definition of Acids and Bases

The first person to define acids and bases in detail was the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry, 1903). According to the *Arrhenius definition*, an acid is a substance like hydrochloric acid that dissolves in water to produce H^+ ions (protons; Equation 9.7.1), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions (Equation 9.7.2):

$$\underset{an\ Arrhenius\ acid}{HCl_{(g)}} \xrightarrow{H_2O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)} \tag{9.7.1}$$

$$\underset{an\ Arrhenius\ base}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)} \tag{9.7.2}$$

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 9.7.3) is not an acid–base reaction because it does not involve H^+ and OH^-:

$$NH_{3\ (g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{9.7.3}$$

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 9.7.3, NH_3 is a Brønsted–Lowry base and HCl is a Brønsted–Lowry acid. Because of its more general nature, the Brønsted–Lowry definition is used throughout this text unless otherwise specified.

Polyprotic Acids

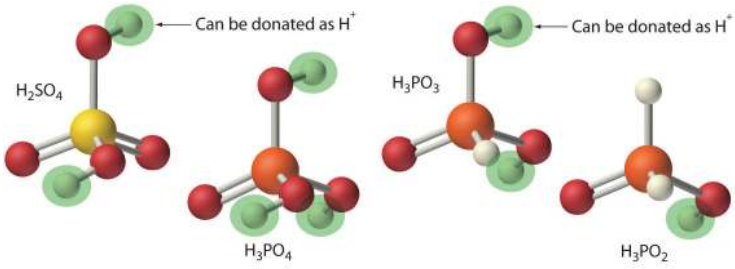
Acids differ in the number of protons they can donate. For example, monoprotic acids (a compound that is capable of donating one proton per molecule) are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF, HCl, HBr, HI, HNO_3, and HNO_2. All carboxylic acids that contain a single $-CO_2H$ group, such as acetic acid (CH_3CO_2H), are monoprotic acids, dissociating to form RCO_2^- and H^+. A compound that can donate more than one proton per molecule is known as a **polyprotic acid**. For example, H_2SO_4 can donate two H^+ ions in separate steps, so it is a diprotic acid (a compound that can donate two protons per molecule in separate steps) and H_3PO_4, which is capable of donating three protons in successive steps, is a triprotic acid (a compound that can donate three protons per molecule in separate steps), (Equation 9.7.4, Equation 9.7.5, and Equation 9.7.6):

$$H_3PO_4(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + H_2PO_4^-(aq) \tag{9.7.4}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \tag{9.7.5}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \tag{9.7.6}$$

In chemical equations such as these, a double arrow is used to indicate that both the forward and reverse reactions occur simultaneously, so the forward reaction does not go to completion. Instead, the solution contains significant amounts of both reactants and products. Over time, the reaction reaches a state in which the concentration of each species in solution remains constant. The reaction is then said to be in **equilibrium** (the point at which the rates of the forward and reverse reactions become the same, so that the net composition of the system no longer changes with time).



Ball and stick diagram of sulfuric acid, phosporic acid, phosphorous acid, and hypophosphorous acid with all of the hydrogen atoms highlighted to show availability to be donated as H positive ion.

Strengths of Acids and Bases

We will not discuss the strengths of acids and bases quantitatively until next semester. Qualitatively, however, we can state that **strong acids** react essentially completely with water to give H^+ and the corresponding anion. Similarly, **strong bases** dissociate essentially completely in water to give OH^- and the corresponding cation. Strong acids and strong bases are both strong electrolytes. In contrast, only a fraction of the molecules of weak acids and weak bases react with water to produce ions, so weak

acids and weak bases are also weak electrolytes. Typically less than 5% of a weak electrolyte dissociates into ions in solution, whereas more than 95% is present in undissociated form.

In practice, only a few strong acids are commonly encountered: HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4 (H_3PO_4 is only moderately strong). The most common strong bases are ionic compounds that contain the hydroxide ion as the anion; three examples are NaOH, KOH, and $Ca(OH)_2$. Common weak acids include HCN, H_2S, HF, oxoacids such as HNO_2 and HClO, and carboxylic acids such as acetic acid. The ionization reaction of acetic acid is as follows:

$$CH_3CO_2H(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + CH_3CO_2^-(aq) \tag{9.7.7}$$

Although acetic acid is *very* soluble in water, almost all of the acetic acid in solution exists in the form of neutral molecules (less than 1% dissociates). Sulfuric acid is unusual in that it is a strong acid when it donates its first proton (Equation 9.7.8) but a weak acid when it donates its second proton (Equation 9.7.9) as indicated by the single and double arrows, respectively:

$$\underset{strong\ acid}{H_2SO_4(l)} \xrightarrow{H_2O(l)} H^+(aq) + HSO_4^-(aq) \tag{9.7.8}$$

$$\underset{weak\ acid}{HSO_4^-(aq)} \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \tag{9.7.9}$$

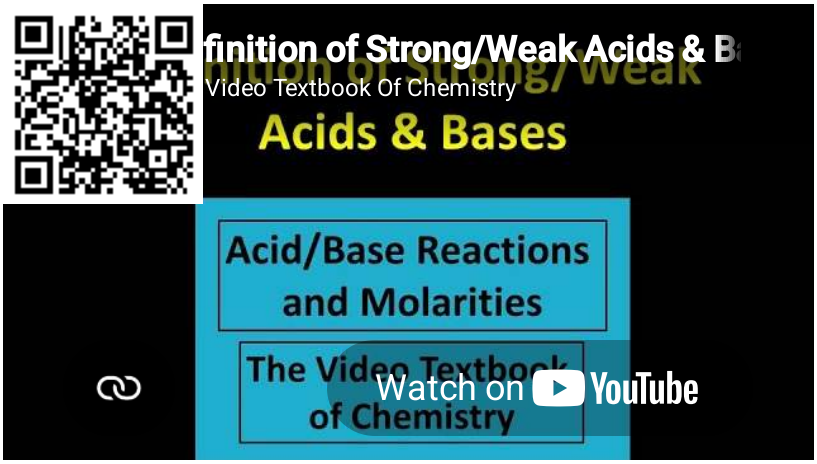
Consequently, an aqueous solution of sulfuric acid contains $H^+_{(aq)}$ ions and a mixture of $HSO^-_{4\ (aq)}$ and $SO^{2-}_{4\ (aq)}$ ions, but no H_2SO_4 molecules. All other polyprotic acids, such as H_3PO_4, are weak acids.

The most common weak base is ammonia, which reacts with water to form small amounts of hydroxide ion:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{9.7.10}$$

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.*



Definition of Strong/Weak Acids & Bases: Definition of Strong/Weak Acids & Bases, YouTube (opens in new window) [Definition of Strong] [Definition of Strong] [youtu.be] (opens in new window)

Table 9.7.1 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 9.7.1: Common Strong Acids and Bases

Strong Acids		Strong Bases	
Hydrogen Halides	Oxoacids	Group 1 Hydroxides	Hydroxides of Heavy Group 2 Elements
HCl	HNO_3	LiOH	$Ca(OH)_2$
HBr	H_2SO_4	NaOH	$Sr(OH)_2$
HI	$HClO_4$	KOH	$Ba(OH)_2$
		RbOH	
		CsOH	

Example 9.7.1: Acid Strength

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

a. $CH_3CH_2CO_2H$
b. CH_3OH
c. $Sr(OH)_2$
d. $CH_3CH_2NH_2$
e. $HBrO_4$

Given: compound

Asked for: acid or base strength

Strategy:

A Determine whether the compound is organic or inorganic.

B If inorganic, determine whether the compound is acidic or basic by the presence of dissociable H^+ or OH^- ions, respectively. If organic, identify the compound as a weak base or a weak acid by the presence of an amine or a carboxylic acid group, respectively. Recall that all polyprotic acids except H_2SO_4 are weak acids.

Solution:

a. **A** This compound is propionic acid, which is organic. **B** It contains a carboxylic acid group analogous to that in acetic acid, so it must be a weak acid.
b. **A** CH_3OH is methanol, an organic compound that contains the −OH group. **B** As a covalent compound, it does not dissociate to form the OH^- ion. Because it does not contain a carboxylic acid ($-CO_2H$) group, methanol also cannot dissociate to form $H^+(aq)$ ions. Thus we predict that in aqueous solution methanol is neither an acid nor a base.
c. **A** $Sr(OH)_2$ is an inorganic compound that contains one Sr^{2+} and two OH^- ions per formula unit. **B** We therefore expect it to be a strong base, similar to $Ca(OH)_2$.
d. **A** $CH_3CH_2NH_2$ is an amine (ethylamine), an organic compound in which one hydrogen of ammonia has been replaced by an R group. **B** Consequently, we expect it to behave similarly to ammonia (Equation 9.7.7), 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 9.7.1 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 9.7.1: Acid Strength

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

a. $Ba(OH)_2$

b. HIO_4
c. $CH_3CH_2CH_2CO_2H$
d. $(CH_3)_2NH$
e. CH_2O

Answer a

strong base

Answer b

strong acid

Answer c

weak acid

Answer d

weak base

Answer e

none of these; formaldehyde is a neutral molecule

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9.8: Gas-Evolution Reactions



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9.9: Oxidation-Reduction Reactions

Learning Objectives

- To identify oxidation–reduction reactions in solution.

The term oxidation was first used to describe reactions in which metals react with oxygen in air to produce metal oxides. When iron is exposed to air in the presence of water, for example, the iron turns to rust—an iron oxide. When exposed to air, aluminum metal develops a continuous, transparent layer of aluminum oxide on its surface. In both cases, the metal acquires a positive charge by transferring electrons to the neutral oxygen atoms of an oxygen molecule. As a result, the oxygen atoms acquire a negative charge and form oxide ions (O^{2-}). Because the metals have lost electrons to oxygen, they have been oxidized; oxidation is therefore the loss of electrons. Conversely, because the oxygen atoms have gained electrons, they have been reduced, so reduction is the gain of electrons. For every oxidation, there must be an associated reduction. Therefore, these reactions are known as oxidation-reduction reactions, or "redox" reactions for short.

> *Any oxidation must ALWAYS be accompanied by a reduction and vice versa.*

Originally, the term reduction referred to the decrease in mass observed when a metal oxide was heated with carbon monoxide, a reaction that was widely used to extract metals from their ores. When solid copper(I) oxide is heated with hydrogen, for example, its mass decreases because the formation of pure copper is accompanied by the loss of oxygen atoms as a volatile product (water vapor). The reaction is as follows:

$$\mathrm{Cu_2O\,(s) + H_2\,(g)\ \rightarrow 2\,Cu\,(s) + H_2O\,(g)} \tag{9.9.1}$$

Oxidation-reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants by a transfer of electrons, which follows the mnemonic "oxidation is loss, reduction is gain", or **"oil rig"**. The **oxidation state** of each atom in a compound is the charge an atom would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. Atoms in their elemental form, such as O_2 or H_2, are assigned an oxidation state of zero. For example, the reaction of aluminum with oxygen to produce aluminum oxide is

$$\mathrm{4\,Al\,(s) + 3\,O_2\ \rightarrow 2\,Al_2O_3\,(s)} \tag{9.9.2}$$

Each neutral oxygen atom gains two electrons and becomes negatively charged, forming an oxide ion; thus, oxygen has an oxidation state of −2 in the product and has been reduced. Each neutral aluminum atom loses three electrons to produce an aluminum ion with an oxidation state of +3 in the product, so aluminum has been oxidized. In the formation of Al_2O_3, electrons are transferred as follows (the small overset number emphasizes the oxidation state of the elements):

$$\mathrm{4\overset{0}{Al} + 3\overset{0}{O_2} \rightarrow 4\,Al^{3+} + 6\,O^{2-}} \tag{9.9.3}$$

Equation 9.9.1 and Equation 9.9.2 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 9.9.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$\begin{aligned}\text{electrons lost} &= 4\,\text{Al atoms} \times \frac{3\,e^-\,\text{lost}}{\text{Al atom}} \\ &= 12\,e^-\,\text{lost}\end{aligned}$$

$$\begin{aligned}\text{electrons gained} &= 6\,\text{O atoms} \times \frac{2\,e^-\,\text{gained}}{\text{O atom}} \\ &= 12\,e^-\,\text{gained}\end{aligned}$$

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained. An additional example of a redox reaction, the reaction of sodium metal with chlorine is illustrated in Figure 9.9.1.

> *In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.*

Assigning Oxidation States

Assigning oxidation states to the elements in binary ionic compounds is straightforward: the oxidation states of the elements are identical to the charges on the monatomic ions. Previously, you learned how to predict the formulas of simple ionic compounds based on the sign and magnitude of the charge on monatomic ions formed by the neutral elements. Examples of such compounds are sodium chloride (NaCl; Figure 9.9.1), magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. However, we can still assign oxidation states to the elements involved by treating them as if they were ionic (that is, as if all the bonding electrons were transferred to the more attractive element). Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

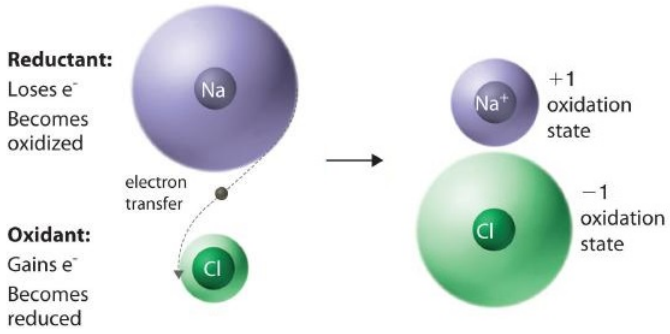


Figure 9.9.1: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.

Sodium atom acts as the reductant and chlorine as the oxidant. The result is an oxidation state of positive 1 and negative 1 for sodium and chloride ion respectively.

A set of rules for assigning oxidation states to atoms in chemical compounds follows.

Rules for Assigning Oxidation States

1. The oxidation state of an atom in any pure element, whether monatomic, diatomic, or polyatomic, is zero.
2. The oxidation state of a monatomic ion is the same as its charge—for example, $Na^+ = +1$, $Cl^- = -1$.
3. The oxidation state of fluorine in chemical compounds is always −1. Other halogens usually have oxidation states of −1 as well, except when combined with oxygen or other halogens.
4. Hydrogen is assigned an oxidation state of +1 in its compounds with nonmetals and −1 in its compounds with metals.
5. Oxygen is normally assigned an oxidation state of −2 in compounds, with two exceptions: in compounds that contain oxygen–fluorine or oxygen–oxygen bonds, the oxidation state of oxygen is determined by the oxidation states of the other elements present.
6. The sum of the oxidation states of all the atoms in a neutral molecule or ion must equal the charge on the molecule or ion.

> *Nonintegral (fractional) oxidation states are encountered occasionally. They are usually due to the presence of two or more atoms of the same element with different oxidation states.*

In any chemical reaction, the net charge must be conserved; that is, in a chemical reaction, the total number of electrons is constant, just like the total number of atoms. Consistent with this, rule 1 states that the sum of the individual oxidation states of the atoms in a molecule or ion must equal the net charge on that molecule or ion. In NaCl, for example, Na has an oxidation state of +1 and Cl is −1. The net charge is zero, as it must be for any compound.

Rule 3 is required because fluorine attracts electrons more strongly than any other element, for reasons you will discover in Chapter 6. Hence fluorine provides a reference for calculating the oxidation states of other atoms in chemical compounds. Rule 4 reflects the difference in chemistry observed for compounds of hydrogen with nonmetals (such as chlorine) as opposed to compounds of

hydrogen with metals (such as sodium). For example, NaH contains the H^- ion, whereas HCl forms H^+ and Cl^- ions when dissolved in water. Rule 5 is necessary because fluorine has a greater attraction for electrons than oxygen does; this rule also prevents violations of rule 2. So the oxidation state of oxygen is +2 in OF_2 but −½ in KO_2. Note that an oxidation state of −½ for O in KO_2 is perfectly acceptable.

The reduction of copper(I) oxide shown in Equation 9.9.4 demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to H_2 and Cu. From rule 4, hydrogen in H_2O has an oxidation state of +1, and from rule 5, oxygen in both Cu_2O and H_2O has an oxidation state of −2. Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in Cu_2O must have a charge of +1: 2(+1) + (−2) = 0. So the oxidation states are as follows:

$$\overset{+1\ -2}{\mathrm{Cu_2O}}(s) + \overset{0}{\mathrm{H_2}}(g) \rightarrow 2\overset{0}{\mathrm{Cu}}(s) + \overset{+1\ -2}{\mathrm{H_2O}}(g) \tag{9.9.4}$$

Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen (0 → +1) to copper (+1 → 0). Thus, this is a redox reaction. Once again, the number of electrons lost equals the number of electrons gained, and there is a net conservation of charge:

$$\text{electrons lost} = 2\,H\,\text{atoms} \times \frac{1\,e^-\,\text{lost}}{H\,\text{atom}} = 2\,e^-\,\text{lost} \tag{9.9.5}$$

$$\text{electrons gained} = 2\,Cu\,\text{atoms} \times \frac{1\,e^-\,\text{gained}}{Cu\,\text{atom}} = 2\,e^-\,\text{gained} \tag{9.9.6}$$

Remember that oxidation states are useful for visualizing the transfer of electrons in oxidation–reduction reactions, but the oxidation state of an atom and its actual charge are the same only for simple ionic compounds. Oxidation states are a convenient way of assigning electrons to atoms, and they are useful for predicting the types of reactions that substances undergo.

Example 9.9.1: Oxidation States

Assign oxidation states to all atoms in each compound.

a. sulfur hexafluoride (SF_6)
b. methanol (CH_3OH)
c. ammonium sulfate [$(NH_4)2SO_4$]
d. magnetite (Fe_3O_4)
e. ethanoic (acetic) acid (CH_3CO_2H)

Given: molecular or empirical formula

Asked for: oxidation states

Strategy:

Begin with atoms whose oxidation states can be determined unambiguously from the rules presented (such as fluorine, other halogens, oxygen, and monatomic ions). Then determine the oxidation states of other atoms present according to rule 1.

Solution:

a. We know from rule 3 that fluorine always has an oxidation state of −1 in its compounds. The six fluorine atoms in sulfur hexafluoride give a total negative charge of −6. Because rule 1 requires that the sum of the oxidation states of all atoms be zero in a neutral molecule (here SF_6), the oxidation state of sulfur must be +6:

[(6 F atoms)(−1)] + [(1 S atom) (+6)] = 0

b. According to rules 4 and 5, hydrogen and oxygen have oxidation states of +1 and −2, respectively. Because methanol has no net charge, carbon must have an oxidation state of −2:

[(4 H atoms)(+1)] + [(1 O atom)(−2)] + [(1 C atom)(−2)] = 0

c. Note that $(NH_4)_2SO_4$ is an ionic compound that consists of both a polyatomic cation (NH_4^+) and a polyatomic anion (SO_4^{2-}) (see Table 2.4). We assign oxidation states to the atoms in each polyatomic ion separately. For NH_4^+, hydrogen has an

oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of −3:

$$[(4\text{ H atoms})(+1)] + [(1\text{ N atom})(-3)] = +1, \text{ the charge on the } NH_4^+ \text{ ion}$$

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:

$$[(4\text{ O atoms})(-2)]+[(3\text{ Fe atoms})(+\tfrac{8}{3})]= 0$$

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

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

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

? Exercise 9.9.1: Oxidation States

Assign oxidation states to all atoms in each compound.

a. barium fluoride (BaF_2)
b. formaldehyde (CH_2O)
c. potassium dichromate ($K_2Cr_2O_7$)
d. cesium oxide (CsO_2)
e. ethanol (CH_3CH_2OH)

Answer a

Ba, +2; F, −1

Answer b

C, 0; H, +1; O, −2

Answer c

K, +1; Cr, +6; O, −2

Answer d

Cs, +1; O, −½

Answer e

C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

Types of Redox Reactions

Many types of chemical reactions are classified as redox reactions, and it would be impossible to memorize all of them. However, there are a few important types of redox reactions that you are likely to encounter and should be familiar with. These include:

- **Synthesis** reactions: The formation of any compound directly from the elements is a redox reaction, for example, the formation of water from hydrogen and oxygen:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

- **Decomposition** reactions: Conversely, the decomposition of a compound to its elements is also a redox reaction, as in the electrolysis of water:

$$2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g)$$

- **Combustion** reactions: Many chemicals combust (burn) with oxygen. In particular, organic chemicals such as hydrocarbons burn in the presence of oxygen to produce carbon dioxide and water as the products:

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

The following sections describe another important class of redox reactions: single-displacement reactions of metals in solution.

Redox Reactions of Solid Metals in Aqueous Solution

- A widely encountered class of oxidation–reduction reactions is the reaction of aqueous solutions of acids or metal salts with solid metals. An example is the corrosion of metal objects, such as the rusting of an automobile (Figure 9.9.2). Rust is formed from a complex oxidation–reduction reaction involving dilute acid solutions that contain Cl^- ions (effectively, dilute HCl), iron metal, and oxygen. When an object rusts, iron metal reacts with HCl(aq) to produce iron(II) chloride and hydrogen gas:

$$Fe\,(s) + 2\,HCl\,(aq) \rightarrow FeCl_2\,(aq) + H_2\,(g) \tag{9.9.7}$$

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



Figure 9.9.2: Rust Formation. The corrosion process involves an oxidation–reduction reaction in which metallic iron is converted to $Fe(OH)_3$, a reddish-brown solid.

Many metals dissolve through reactions of this type, which have the general form

$$\text{metal} + \text{acid} \rightarrow \text{salt} + \text{hydrogen} \tag{9.9.8}$$

Some of these reactions have important consequences. For example, it has been proposed that one factor that contributed to the fall of the Roman Empire was the widespread use of lead in cooking utensils and pipes that carried water. Rainwater, as we have seen, is slightly acidic, and foods such as fruits, wine, and vinegar contain organic acids. In the presence of these acids, lead dissolves:

$$\mathrm{Pb\,(s) + 2\,H^+\,(aq)} \rightarrow \mathrm{Pb^{2+}\,(aq) + H_2\,(g)} \tag{9.9.9}$$

Consequently, it has been speculated that both the water and the food consumed by Romans contained toxic levels of lead, which resulted in widespread lead poisoning and eventual madness. Perhaps this explains why the Roman Emperor Caligula appointed his favorite horse as consul!

Single-Displacement Reactions

Certain metals are oxidized by aqueous acid, whereas others are oxidized by aqueous solutions of various metal salts. Both types of reactions are called single-displacement reactions, in which the ion in solution is displaced through oxidation of the metal. Two examples of single-displacement reactions are the reduction of iron salts by zinc (Equation 9.9.10) and the reduction of silver salts by copper (Equation 9.9.11 and Figure 9.9.3):

$$\mathrm{Zn\,(s) + Fe^{2+}\,(aq)} \rightarrow \mathrm{Zn^{2+}\,(aq) + Fe\,(s)} \tag{9.9.10}$$

$$\mathrm{Cu\,(s) + 2\,Ag^{+}\,(aq)} \rightarrow \mathrm{Cu^{2+}\,(aq) + 2\,Ag\,(s)} \tag{9.9.11}$$

The reaction in Equation 9.9.10 is widely used to prevent (or at least postpone) the corrosion of iron or steel objects, such as nails and sheet metal. The process of “galvanizing” consists of applying a thin coating of zinc to the iron or steel, thus protecting it from oxidation as long as zinc remains on the object.



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The Activity Series

By observing what happens when samples of various metals are placed in contact with solutions of other metals, chemists have arranged the metals according to the relative ease or difficulty with which they can be oxidized in a single-displacement reaction. For example, metallic zinc reacts with iron salts, and metallic copper reacts with silver salts. Experimentally, it is found that zinc reacts with both copper salts and silver salts, producing $\mathrm{Zn_2{}^+}$. Zinc therefore has a greater tendency to be oxidized than does iron, copper, or silver. Although zinc will not react with magnesium salts to give magnesium metal, magnesium metal will react with zinc salts to give zinc metal:

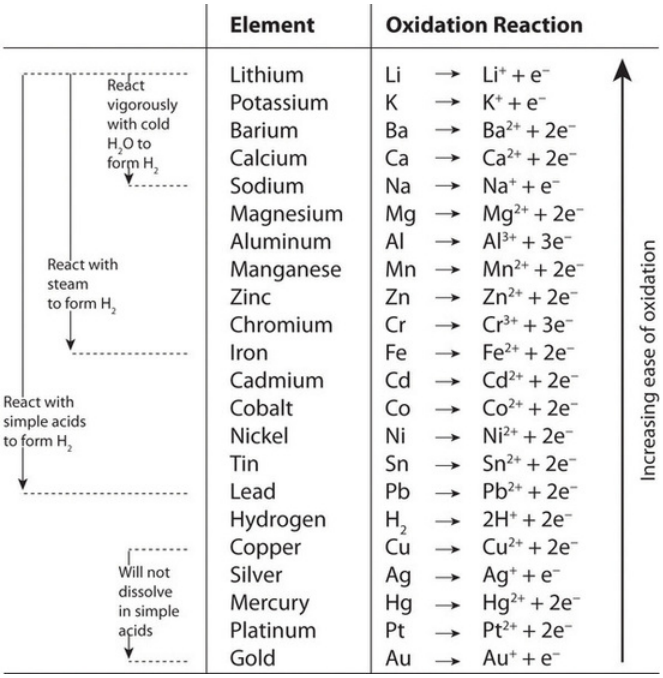
$$\mathrm{Zn\,(s) + Mg^{2+}\,(aq)} \not\rightarrow \mathrm{Zn^{2+}\,(aq) + Mg\,(s)} \tag{9.9.12}$$

$$\mathrm{Mg\,(s) + Zn^{2+}\,(aq)} \rightarrow \mathrm{Mg^{2+}\,(aq) + Zn\,(s)} \tag{9.9.13}$$

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

Pairwise reactions of this sort are the basis of the activity series (Figure 9.9.4), 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 9.9.4: 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 9.9.4, 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 9.9.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

✔ Example 9.9.2: Activity

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

a. A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
b. A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
c. Some sulfuric acid from a car battery is accidentally spilled on the lead cable terminals.

Given: reactants

Asked for: overall reaction and net ionic equation

Strategy:

A. Locate the reactants in the activity series in Figure 9.9.4 and from their relative positions, predict whether a reaction will occur. If a reaction does occur, identify which metal is oxidized and which is reduced.
B. Write the net ionic equation for the redox reaction.

Solution:

1. **A** Aluminum is an active metal that lies above silver in the activity series, so we expect a reaction to occur. According to their relative positions, aluminum will be oxidized and dissolve, and silver ions will be reduced to silver metal. **B** The net ionic equation is as follows:

$$\mathrm{Al(s) + 3\,Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3\,Ag(s)}$$

   Recall from our discussion of solubilities that most nitrate salts are soluble. In this case, the nitrate ions are spectator ions and are not involved in the reaction.

2. **A** Mercury lies below lead in the activity series, so no reaction will occur.
3. **A** Lead is above hydrogen in the activity series, so the lead terminals will be oxidized, and the acid will be reduced to form H_2. **B** From our discussion of solubilities, recall that Pb^{2+} and SO_4^{2-} form insoluble lead(II) sulfate. In this case, the sulfate ions are *not* spectator ions, and the reaction is as follows:

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

   Lead(II) sulfate is the white solid that forms on corroded battery terminals.



Corroded battery terminals. *The white solid is lead(II) sulfate, formed from the reaction of solid lead with a solution of sulfuric acid.*

? Exercise 9.9.2

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

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

Answer a

no reaction

Answer b

$3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$

Answer c

\(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 9.9.1), in which the overall reaction is separated into an oxidation equation and a reduction equation. There are many types of redox reactions. **Single-displacement reactions** are reactions of metals with either acids or another metal salt that result in dissolution of the first metal and

precipitation of a second (or evolution of hydrogen gas). The outcome of these reactions can be predicted using the **activity series** (Figure 9.9.4), 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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CHAPTER OVERVIEW

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10.1: On Fire, But Not Consumed



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10.2: The Nature of Energy - Key Definitions

; the potential energies of electrons in the force field created by atomic nuclei lie at the heart of the chemical behavior of and molecules. "" usually refers to the energy that is stored in the of molecules. These bonds form when electrons are able to respond to the force fields created by two or more atomic nuclei, so they can be regarded as manifestations of electrostatic potential energy. In an chemical reaction, the electrons and nuclei within the reactants undergo rearrangement into products possessing lower energies, and the difference is released to the environment in the form of heat. chemical reaction heats surrounding , the kinetic energy gets dispersed into the molecular units in the environment. This "microscopic" form of kinetic energy, unlike that of a speeding bullet, is completely random in the kinds of motions it exhibits and in its direction. We refer to this as "thermalized" kinetic energy, or more commonly simply as . We observe the effects of this as a rise in the temperature of the . The temperature of a body is direct measure of the quantity of thermal energy is contains. , energy comes in different types. Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the : (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car’s engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders’ pistons. The is also one version of the first law of thermodynamics, as you will learn later. in glucose to keep us warm and to move our muscles. In fact, life itself depends on the conversion of to other forms. So when you go uphill, your kinetic energy is transformed into potential energy, which gets changed back into kinetic energy as you coast down the other side. And where did the kinetic energy you expended in peddling uphill come from? By conversion of some of the chemical potential energy in your breakfast cereal.). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (or first law of thermodynamics). has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat () or release heat (). The SI unit of energy, heat, and work is the .

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10.3: The First Law of Thermodynamics - There Is No Free Lunch

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 10.3.1). 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.

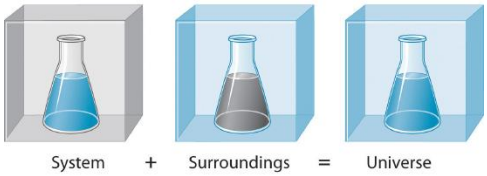


Figure 10.3.1: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

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 10.3.2). 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 10.3.2: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions.

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (Figure 10.3.3). The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al}\,(\mathrm{s}) + \mathrm{Fe_2O_3}\,(\mathrm{s}) \longrightarrow 2\,\mathrm{Fe}\,(\mathrm{s}) + \mathrm{Al_2O_3}\,(\mathrm{s}) \tag{10.3.1}$$



Figure 10.3.3: The thermite reaction produces so much heat that the iron it produces comes out molten, a property that makes this reaction useful in welding. Image by Kingfisher [CC BY-SA 3.0 (Creative Commons [creativecommons.org])], from Wikimedia Commons.

We can also write this chemical equation as

$$2\,\mathrm{Al}\,(\mathrm{s}) + \mathrm{Fe_2O_3}\,(\mathrm{s}) \;\rightarrow 2\,\mathrm{Fe}\,(\mathrm{s}) + \mathrm{Al_2O_3}\,(\mathrm{s}) + \mathrm{heat} \tag{10.3.2}$$

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:

$$\mathrm{heat} + \mathrm{H_2O}\,(\mathrm{s}) \;\rightarrow \mathrm{H_2O}\,(\mathrm{l}) \tag{10.3.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a $heat$ term in the chemical reaction like in Equations 10.3.2 and 10.3.3 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:

$$U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{10.3.4}$$

$$\Delta U_{sys} = -\Delta U_{surr} \tag{10.3.5}$$

where the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/ O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta U_{sys} = q + w \tag{10.3.6}$$

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed.

Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a state function.

Thus, because of the first law, we can determine ΔU for any process if we can measure both q and w. Heat, q, may be calculated by measuring a change in temperature of the surroundings. Work, w, may come in different forms, but it too can be measured. One important form of work for chemistry is *pressure-volume work* done by an expanding gas. At a constant external pressure (for example, atmospheric pressure)

$$w = -P\Delta V \tag{10.3.7}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. That is, an expanding gas does work on its surroundings, while a gas that is compressed has work done on it by the surroundings.

Example 10.3.1

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 10.3.6.

B. From Equation 10.3.7 calculate w from the values given. Substitute this value into Equation 10.3.6 to calculate ΔU.

Solution

A From Equation 10.3.6, we know that ΔU = q + w. We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 10.3.6,

$$w = -P_{\text{ext}}\Delta V = -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L}\cdot\text{atm}}\right) = 284\ \text{J}$$

Thus

$$\begin{aligned}\Delta U &= q + w \\ &= -140\ J + 284\ J \\ &= 144\ J\end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise 10.3.1

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

By convention (to chemists), both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**. The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

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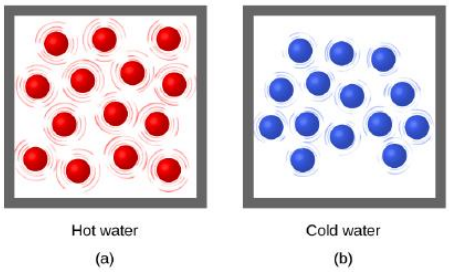
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10.4: Quantifying Heat and Work

Learning Objectives

- To calculate changes in internal energy
- 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

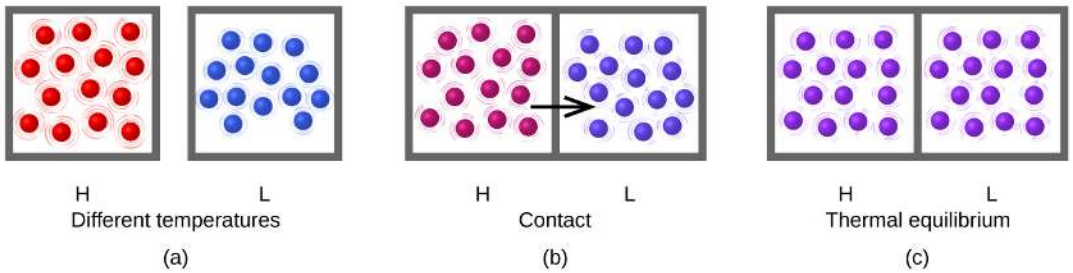
Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is “hot.” When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is “cold” (Figure 10.4.1). 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.



Drawing a is a box containing red spheres that are surrounded by lines indicating that the particles are moving rapidly. Drawing b depicts another box which also contains spheres, but these are blue. They are all surrounded by smaller lines that depict a slower motion compared to drawing a.

Figure 10.4.1: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

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 10.4.2).



Drawing a shows two separated boxes with red and blue spheres respectively. The radial lines along each sphere are more concentrated for the box containing hotter molecules. Drawing b shows the two boxes in contact as well as the direction of heat transfer from the hotter to colder region. The colors of the two molecules are turning into two different shades of maroon. The final drawing depicts two boxes where molecules in each box are exactly identical in terms of color and motion.

Figure 10.4.2: (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 10.4.3*a*). 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.



Two pictures are shown and labeled a and b. Picture a shows a metal railroad tie being cut with the flame of an acetylene torch. Picture b shows a chemical cold pack containing ammonium nitrate.

Figure 10.4.3: (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.

$$1\,cal \equiv 4.184\,J \tag{10.4.1}$$

Application: Heat can do more than increase temperature

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 10.4.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

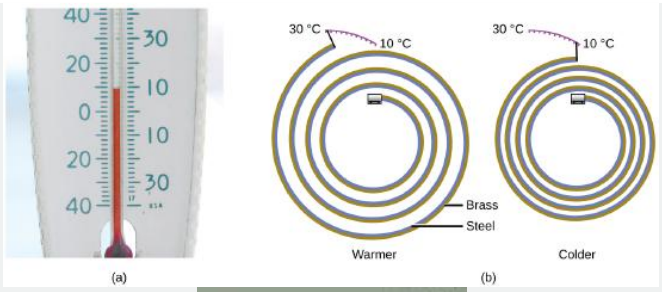




Figure 10.4.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. 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)

Picture a shows the lower portion of an alcohol thermometer. The two images labeled b both depict a metal strip coiled into a spiral and composed of brass and steel. The left coil, which is loosely coiled, is labeled along its upper edge with the 30 degrees C and 10 degrees C. The end of the coil is near the 30 degrees C label. The right hand coil is much more tightly wound and the end is near the 10 degree C label.

Direction of Heat Flow: Endothermic vs. Exothermic Processes

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. The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \tag{10.4.2}$$

We can also write this chemical equation as

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + \mathrm{heat} \tag{10.4.3}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.



When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\text{heat} + \text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)} \tag{10.4.4}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

> *By convention, $q < 0$ for an exothermic reaction and $q > 0$ for an endothermic reaction.*

Exercise 10.4.1

Decide whether the following are endothermic or exothermic processes

a. water evaporates off a shower door
b. an acid tablet being added to a pool and the surrounding water heats up
c. NH_4Cl is dissolved in water and the solution cools
d. the burning of a log in a campfire

Hint

During an endothermic process heat is absorbed from surroundings, causing them to cool, so in every case where there is cooling there is most likely an endothermic process taking place. For exothermic reactions energy is being released to the surroundings and so the surroundings feel like they have been heated by the process.

Answer a

endothermic

Answer b

exothermic

Answer c

endothermic

Answer d

exothermic

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 10.4.3 and 10.4.4 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.

Contributors and Attributions

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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 10.4.5), which is the energy required to move an object a distance d when *opposed* by a force F, such as gravity:

$$w = F\,d \tag{10.4.5}$$

with w is work, F is opposing force, and d is distance.



GIF

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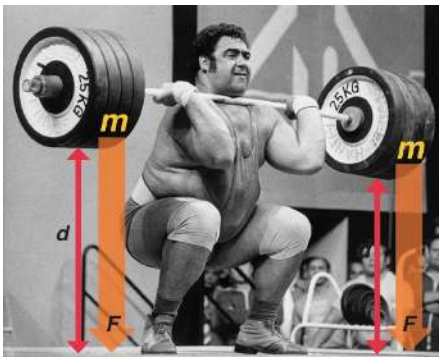


Figure 10.4.5: One form of energy is mechanical work, the energy required to move an object of mass m through distance d when opposed by a force F, i.e., as gravity.

A powerlifter in the middle of lifting a barbell bar with multiple weights attached on each side. The weights are labeled m and an arrow labeled F is shown pointing downwards. The height of the weights from the ground is labeled d.

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), Equation 10.4.5 can be rewritten to:

$$w = m\,a\,d \tag{10.4.6}$$

with w is work, m is mass, a is acceleration, and d is distance.

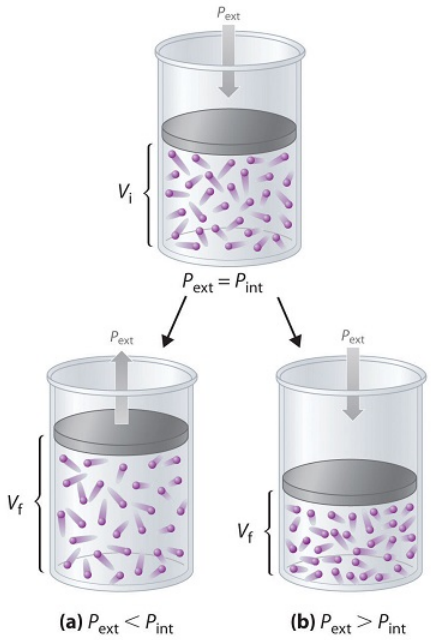
Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth. Hence for works against gravity (on Earth), a can be set to $g = 9.8\ m/s^2$). Consider the mechanical work required for you to travel from the first floor of a building to the second. 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 10.4.6). 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.



The three diagrams which represents the different cases show gaseos molecules shown as spheres in motion in an enclosed cylinder with piston acting from above. The top diagram shows the equilibrium case while the two diagram below it shows cases where external pressure is not equal to internal pressure.

Figure 10.4.6: 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:

$$P_{ext} = \frac{F}{A} \tag{10.4.7}$$

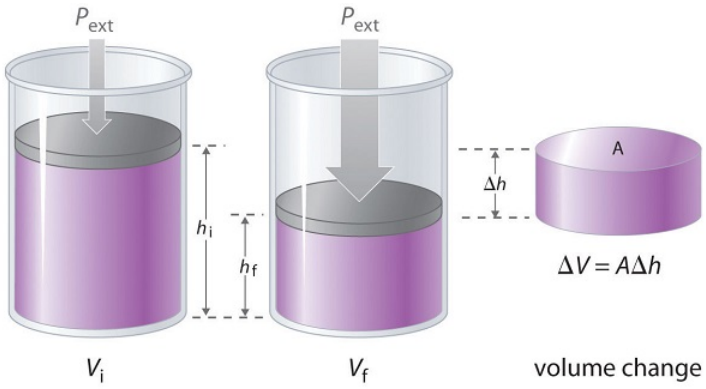
The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging Equation 10.4.7 to give

$$F = P_{ext}A \tag{10.4.8}$$

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 10.4.5:

$$w = Fd = P_{ext}A\Delta h \tag{10.4.9}$$

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is $\Delta V = A\Delta h$, as shown in Figure 10.4.7.



A cylinder containing an initial volume of fluid has a height labeled h subscript i and volume V subscript i. The following diagram shows a compressed volume labeled V subscript f and height of fluid h subscript f. The diagram on the right shows the cylindrical portion of fluid which represents the change in volume as a result of the piston pushing down. It has height of delta h and area A.

Figure 10.4.7: 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 10.4.10.

The PV work performed is thus

$$w = P_{ext}\Delta V \tag{10.4.10}$$

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

$$w = \left(\frac{F}{A}\right)_{\text{ext}}(\Delta V) = \frac{\text{newton}}{\text{m}^2} \times \text{m}^3 = \text{newton} \cdot \text{m} = \text{joule} \tag{10.4.11}$$

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:

$$R = \frac{0.08206\ \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{8.314\ \text{J}}{\text{mol} \cdot \text{K}} \tag{10.4.12}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J.

Exercise: Expansion (PV) work

a. How much work is done by a gas that expands from 2 liters to 5 liters against an external pressure of 750 mmHg?
b. 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?
c. How much work is done by a gas (P=1.7 atm, V=1.56 L) that expands against an external pressure of 1.8 atm?

Solution a

$$w = -P\Delta V \tag{10.4.13}$$

$$\Delta V = V_{final} - V_{Initial} = 5\,L - 2\,L = 3L \tag{10.4.14}$$

Convert 750 mmHg to atm:

$$750mmHg * 1/760(atm/mmHg) = 0.9868atm. \tag{10.4.15}$$

$$W = -p\Delta V = -(.9868\,atm)(3\,L) = -2.96\,L\,atm. \tag{10.4.16}$$

Solution b

First we must find the final volume using the ideal gas law:

$$pV = nRT \tag{10.4.17}$$

or

$$V = \frac{nRT}{P} = \frac{[(0.54\,moles)(0.082057(L\,atm)/(mol\,K))(303\,K)]}{1.3\,atm} = 10.33\,L \tag{10.4.18}$$

$$\Delta V = V_{final} - V_{initial} = 10.3\,L - 8\,L = 2.3\,L \tag{10.4.19}$$

$$w = -p\Delta V = -(1.3\,atm)(2.3\,L) = -3\,L\,atm. \tag{10.4.20}$$

Solution c

$$w = -p * \Delta V\backslash) = -(1.8\,atm)\,\Delta V. \tag{10.4.21}$$

Given p_1, V_1, and p_2, find V_2: $p_1V_1 = p_2V_2$ (at constant T and n)

$V_2 = (V_1 * P_1)/P_2$ = (1.56 L * 1.7 atm) / 1.8 atm = 1.47 L

Now,

$$\Delta V = V_2 - V_1 = 1.47\,L - 1.56\,L = -0.09 \tag{10.4.22}$$

$$w = -(1.8atm) * (-0.09L) = 0.162Latm. \tag{10.4.23}$$

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 ΔV > 0 for an expansion, Equation 10.4.10 must be written with a negative sign to describe PV work done by the system as negative:

$$w = -P_{ext}\Delta V \tag{10.4.24}$$

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, ΔV < 0 and the work is positive because work is being done on a system by its surroundings.

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.

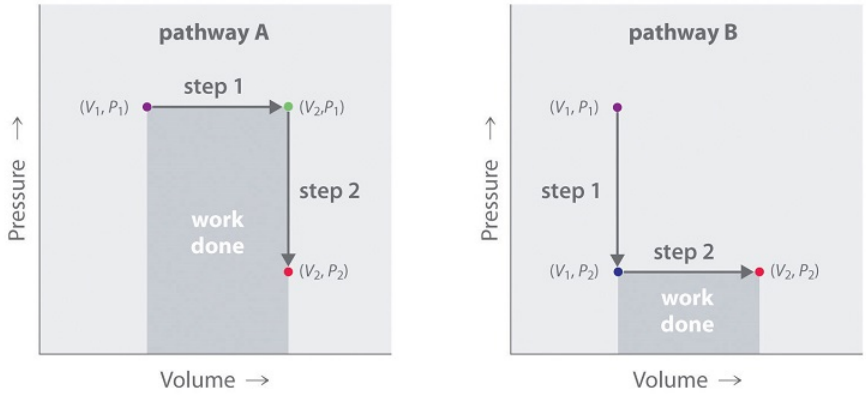


Figure 10.4.8: Work Is Not a State Function. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although (V_1, P_1) and (V_2, P_2) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken.

Two graphs are shown with pressure on the vertical axis and volume on the horizontal axis. Pathway A with arrow pointing right then step 2 has arrow which points from the first arrow straight down. Pathway B has step 1 with arrow pointing straight down then step 2 with an arrow pointing from step 1 straight to the right. The area in pathway A is encompassed by the two arrows. The area in pathway B is found under the step 2 arrow.

In contrast to internal energy, work is not a state function. We can see this by examining Figure 10.4.8, 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.

> *Internal energy is a state function, whereas work is not.*

Example 10.4.1: Internal Combustion Engine

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:

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. Use Equation 10.4.24 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.

$$\begin{aligned} w &= -P_{ext}\Delta V \\ &= -(40.0\,atm)(0.400\,L - 0.0400\,L) \\ &= -14.4\,L \cdot atm \end{aligned}$$

Converting from liter-atmospheres to joules,

$$\begin{aligned} w &= -(14.4\ \text{L} \cdot \text{atm})[101.3\ \text{J}/(\text{L} \cdot \text{atm})] \\ &= -1.46 \times 10^3\ \text{J} \end{aligned}$$

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 10.4.1: Work to Breath

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:

$$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)} \tag{10.4.25}$$

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 10.4.9). 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 (Δ*V*). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V \tag{10.4.26}$$

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.

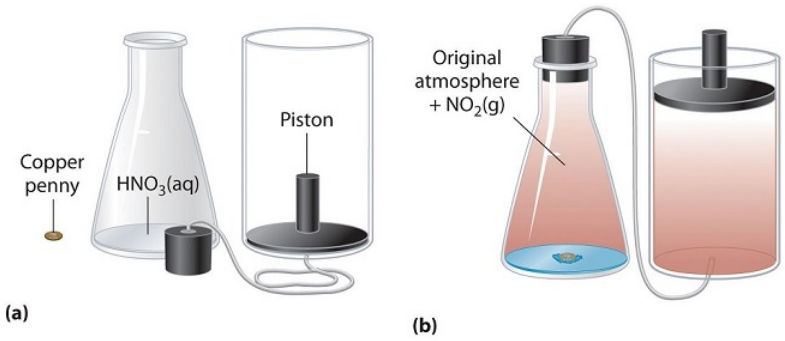


Figure 10.4.9: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

Diagram a shows an Erlenmeyer flask with nitric acid in it and a copper penny beside the flask. A cylidrical container with a piston is shown connected by a tube to a flask stopper. The second diagram shows the copper penny inside the flask and the stopper placed on the neck of the flask. The flask and the cylindrical container is filled with a brownish vapor. The piston is at an elevated position compared to the first diagram since it's pushed upwards by the vapor.

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:

$$H = U + PV \tag{10.4.27}$$

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

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta PV = \Delta U + P\Delta V \tag{10.4.28}$$

Substituting $q + w$ for ΔU (Equation 10.4.28) and $-w$ for $P\Delta V$ (Equation 10.4.26), we obtain

$$\Delta H = \Delta U + P\Delta V = q_p + w - w = q_p \tag{10.4.29}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 10.4.29 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.

$$\Delta H = H_{final} - H_{initial} = q_p \tag{10.4.30}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *To find ΔH for a reaction, measure q_p under constant pressure.*

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.

Outside Links

- Gasparro, Frances P. "Remembering the sign conventions for q and w in deltaU = q - w." J. Chem. Educ. 1976: 53, 389.
- Koubek, E. "PV work demonstration (TD)." J. Chem. Educ. 1980: 57, 374. '

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10.5: Measuring ΔE for Chemical Reactions- 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 10.5.1). 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.

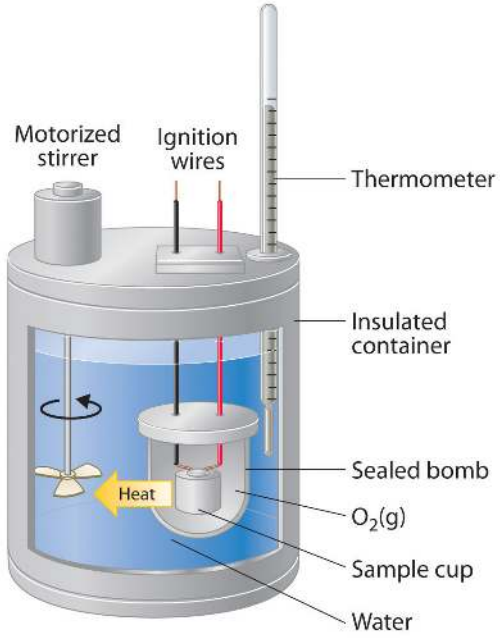


Figure 10.5.1: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.

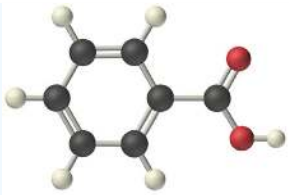
Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔE) rather than the enthalpy change (ΔH); ΔE is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta E < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 10.5.1, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{10.5.1}$$

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 10.5.4.

Example 10.5.4: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation $ref 5.5.9$ to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.

B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 10.5.1 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:

$$qcomb = \left(0.579 \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) = -15.3\ kJ \tag{10.5.2}$$

From Equation 10.5.1,

$$-Cbomb = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^oC} = -7.34\ kJ/^oC \tag{10.5.3}$$

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:

$$q_{comb} = -C_{bomb}\Delta T = \left(-7.34\ kJ/^oC\right)\left(3.64\ ^oC\right) = -26.7\ kJ \tag{10.5.4}$$

Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^3\ kJ/mol \tag{10.5.5}$$

This result is in good agreement (< 1% error) with the value of ΔH_{comb} = −2803 kJ/mol that calculated using enthalpies of formation.

Exercise 10.5.4: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Answer

-1.30×10^3 kJ/mol

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10.6: Enthalpy- The Heat Evolved in a Chemical Reaction at Constant Pressure

Learning Objectives

- To understand how enthalpy pertains to chemical reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just *PV work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$\mathrm{Cu\,(s) + 4\,HNO_3\,(aq)\ \rightarrow Cu(NO_3)_2\,(aq) + 2\,H_2O\,(l) + 2\,NO_2\,(g)}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 10.6.1). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of PV work done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure),

$$w = -P\Delta V \tag{10.6.1}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

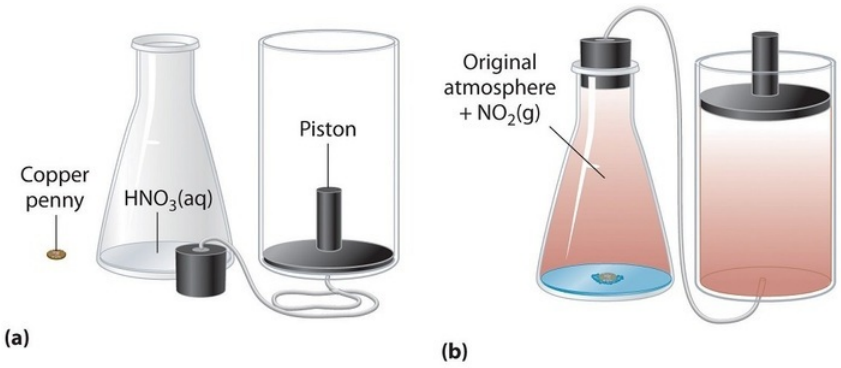


Figure 10.6.1: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings. (CC BY-NC-SA; anonymous)

The internal energy U of a system is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called **enthalpy** (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

\[H =U + PV \label{5.4.3} \]

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function. So we can define a change in enthalpy (ΔH) accordingly

$$\Delta H = H_{final} - H_{initial}$$

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) \tag{10.6.2}$$
$$= \Delta U + \Delta PV \tag{10.6.3}$$
$$= \Delta U + P\Delta V \tag{10.6.4}$$

Substituting $q + w$ for ΔU (First Law of Thermodynamics) and $-w$ for $P\Delta V$ (Equation 10.6.1) into Equation 10.6.4, we obtain

$$\Delta H = \Delta U + P\Delta V \tag{10.6.5}$$
$$= q_p + \cancel{w} - \cancel{w} \tag{10.6.6}$$
$$= q_p \tag{10.6.7}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 10.6.7 we see that at constant pressure the change in enthalpy, ΔH of the system, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} \tag{10.6.8}$$
$$= q_p \tag{10.6.9}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *To find ΔH for a reaction, measure q_p.*

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus:

- $\Delta H_{rxn} < 0$ for an *exothermic reaction*, and
- $\Delta H_{rxn} > 0$ for an *endothermic reaction*.

In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

sign conventions for heat flow and enthalpy changes

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure 10.6.2*a*). 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 10.6.2*b*). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

> *Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.y.*

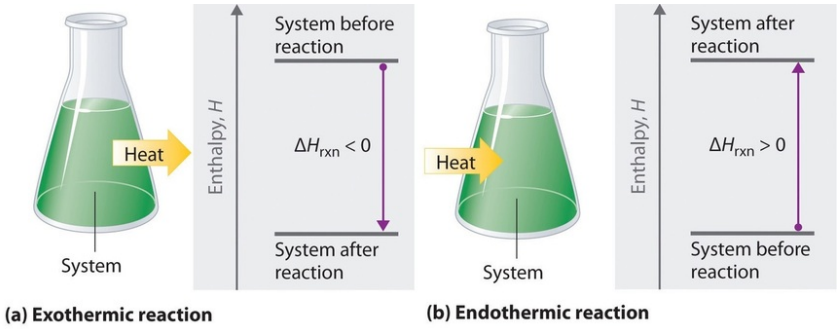


Figure 10.6.2: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill. (CC BY-NC-SA; anonymous)

- **Reversing a reaction or a process changes the sign of Δ*H*.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \quad \Delta H > 0$$

$$H_2O(l) \rightarrow H_2O(s) + heat \quad \Delta H < 0$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 10.6.10, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

$$2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow 2\,Fe\,(s) + Al_2O_3\,(s) + 815.5\ kJ \tag{10.6.10}$$

  Thus Δ*H* = −851.5 kJ/mol of Fe_2O_3. We can also describe Δ*H* 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 Δ*H*, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 10.6.11, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow 2\,Fe\,(s) + Al_2O_3\,(s) \quad \Delta H_{rxn} = -851.5\ kJ \tag{10.6.11}$$

  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:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{10.6.12}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 10.6.1.

✔ Example 10.6.1: Melting Icebergs

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction at 0°C and constant pressure:

$$H_2O\,(s) \longrightarrow H_2O\,(l)$$

How much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \cancel{\text{metric ton}}\ \text{H}_2\text{O}\left(\frac{1000\ \cancel{kg}}{1\ \cancel{\text{metric ton}}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol\,\text{H}_2\text{O}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown below.

Possible sources of the approximately $3.34 \times 10^{11}\ kJ$ needed to melt a 1.00×10^6 metric ton iceberg

- Combustion of 3.8×10^3 ft^3 of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1×10^8 kilowatt-hours of electricity

Alternatively, we can rely on ambient temperatures to slowly melt the iceberg. The main issue with this idea is the cost of dragging the iceberg to the desired place.

? Exercise 10.6.1: Thermite Reaction

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3, how much heat is produced?

Answer

273 kJ

Enthalpies of Reaction

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, since enthalpy is a state function, all we have to know is the initial and final states of the reaction. This allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

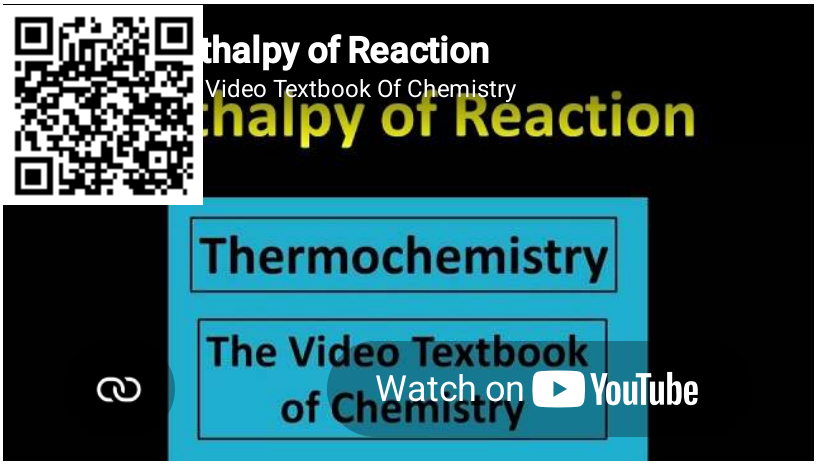
- Enthalpy of combustion (ΔH_{comb}) The change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus}) The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.

- Enthalpy of vaporization (ΔH_{vap}) The enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution (ΔH_{soln}) The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent. The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

Table 10.6.1: 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
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.



Enthalpy of Reaction: Enthalpy of Reaction, YouTube(opens in new window) [youtu.be]

Summary

For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

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10.7: Measuring ΔH for Chemical Reactions- Constant-Pressure Calorimetry

Because Δ*H* 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 Δ*H* 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 10.7.1), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C). Because the heat released or absorbed at constant pressure is equal to Δ*H*, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mC_s\Delta T \tag{10.7.1}$$

The use of a constant-pressure calorimeter is illustrated in Example 10.7.3.

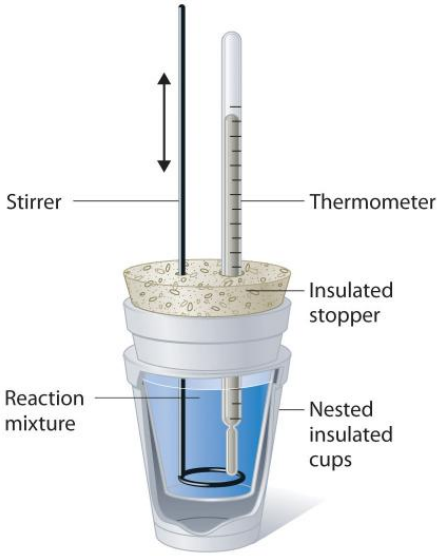


Figure 10.7.1: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants. (CC BY-NC-SA; anonymous)

Example 10.7.1

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 5.5.8.
C. Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$(100.0\ mL\ H2O)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g \tag{10.7.2}$$

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

$$q_{calorimater} = mC_s\Delta T = \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^oC}}\right)(11.7\ ^oC) = 5130\ J = 5.13\ lJ \tag{10.7.3}$$

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 10.7.1, 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:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) = -57.2\ kJ/mol \tag{10.7.4}$$

Exercise 10.7.1

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 10.7.1, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol

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10.8: Relationships Involving ΔHrxn

Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does not depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

> *Hess's Law argues that ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This is nothing more than arguing that ΔH is a state function.*

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 10.8.1 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 5.6.1, the first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation 10.8.1); the enthalpy change for this reaction is −732.5 kJ/mol of Fe_2O_3. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 5.6.1); the enthalpy change for this reaction is −13.8 kJ/mol of Fe (−27.6 kJ per 2 mol Fe). In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation 10.8.1); the enthalpy change for this reaction is −45.5 kJ/mol of Fe (−91.0 kJ per 2 mol Fe). As you can see in Figure 5.6.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 5.6.1 gives the overall reaction, shown in part (d):

$$\begin{array}{rll} 2\,\mathrm{Al(s,25\,^\circ)} + \mathrm{Fe_2O_3(s,25\,^\circ)} \longrightarrow 2\,\mathrm{Fe(l,1758\,^\circ)} + \mathrm{Al_2O_3(s,1758\,^\circ)} & \Delta H = -732.5\,\mathrm{kJ} & \text{(a)} \\ 2\,\mathrm{Fe(l,1758\,^\circ)} \longrightarrow 2\,\mathrm{Fe(s,1758\,^\circ)} & \Delta H = -\ 27.6\,\mathrm{kJ} & \text{(b)} \\ 2\,\mathrm{Fe(s,1758\,^\circ)} + \mathrm{Al_2O_3(s,1758\,^\circ)} \longrightarrow 2\,\mathrm{Fe(s,25\,^\circ)} + \mathrm{Al_2O_3(s,25\,^\circ)} & \Delta H = -\ 91.0\,\mathrm{kJ} & \text{(c)} \\ \hline 2\,\mathrm{Al(s,25\,^\circ)} + \mathrm{Fe_2O_3(s,25\,^\circ)} \longrightarrow \mathrm{Al_2O_3(s,25\,^\circ)} + 2\,\mathrm{Fe(s,25\,^\circ)} & \Delta H = -851.1\,\mathrm{kJ} & \text{(d)} \end{array} \qquad (10.8.1)$$

The net reaction in part (d) in Equation 10.8.1 is identical to the equation for the thermite reaction that we saw in a previous section. By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 10.8.1.

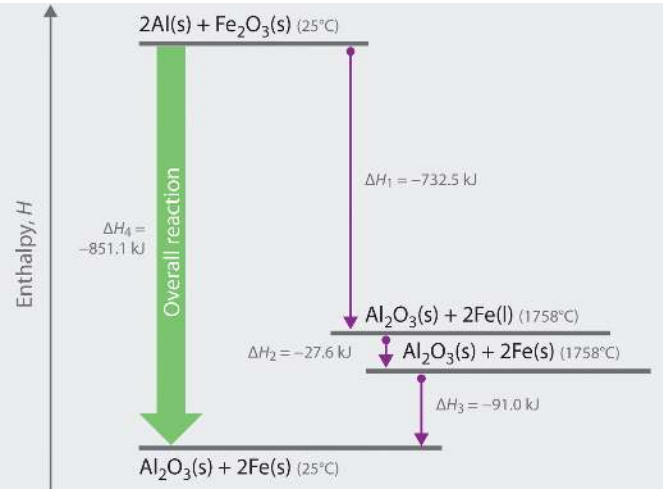


Figure 10.8.1: Energy Changes accompanying the thermite reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical 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 10.8.1 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 10.8.1), 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 10.8.1). 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 10.8.1.
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 10.8.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$(1)\ \ 2\,C\,(s) + O_2\,(g) \longrightarrow 2\,CO\,(g) \quad \Delta H = -221.0\ kJ$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$(2)\ \ C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g) \quad \Delta H = -393.5\ kJ$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A. After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)

B. Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ \ \mathrm{CO\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} \quad \Delta H_{rxn} = ?$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2\,\mathrm{CO\,(g)} \longrightarrow 2\,\mathrm{C\,(s)} + \mathrm{O_2\,(g)} \quad \Delta H = +221.0\ \mathrm{kJ}$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use Equation 2 as written because its product, CO_2, is the product we want in Equation 3:

$$\mathrm{C\,(s)} + \mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(s)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2\,\mathrm{C\,(s)} + 2\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(s)} \quad \Delta H = -787.0\ \mathrm{kJ}$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{lll} 2\,\mathrm{CO\,(g)} \longrightarrow \cancel{2C(s)} + \cancel{O_2(g)} & \Delta H = -\Delta H_1 = +221.0\ \mathrm{kJ} \\ \cancel{2C(s)} + \cancel{2}\ \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)} & \Delta H = -2\Delta H_2 = -787.0\ \mathrm{kJ} \\ \hline 2\,\mathrm{CO\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)} & \Delta H = -566.0\ \mathrm{kJ} \end{array}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount per mole of CO. Consequently, we must divide both sides of the final equation and the magnitude of ΔH by 2:

$$\mathrm{CO\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} \quad \Delta H = -283.0\ \mathrm{kJ}$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{lll} \text{(A)} & 2\,\mathrm{C\,(s)} + \mathrm{O_2\,(g)} \longrightarrow \cancel{2CO(g)} & \Delta H_A = \Delta H_1 = +221.0\ \mathrm{kJ} \\ \text{(B)} & \cancel{2CO(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)} & \Delta H_B = ? \\ \text{(C)} & 2\,\mathrm{C\,(s)} + 2\,\mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)} & \Delta H = 2\Delta H_2 = 2 \times (-393.5\ \mathrm{kJ}) = -787.0\ \mathrm{kJ} \end{array}$$

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 10.8.1

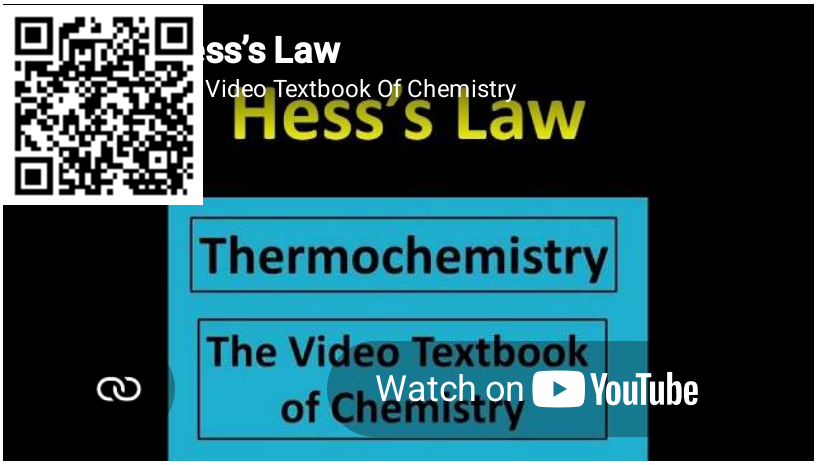
The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2\,(g) + 2H_2\,(g) \rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer

−136.3 kJ/mol of C_2H_4



Hess's Law: Hess's Law, YouTube(opens in new window) [youtu.be]

Summary

Hess's law is arguing the overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions. For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen.

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10.9: Determining Enthalpies of Reaction from Bond Energies

The heat changes which accompany a chemical reaction are caused largely by changes in the electronic energy of the molecules. If we restrict our attention to gases, and hence to fairly simple molecules, we can go quite a long way toward predicting whether a reaction will be exothermic by considering the bonds which are broken and made in the course of the reaction. In order to do this we must first become familiar with the idea of a bond enthalpy.

In other sections we point out that when a chemical bond forms, negative charges move closer to positive charges than before, and so there is a lowering of the energy of the molecule relative to the atoms from which it was made. This means that energy is required to break a molecule into its constituent atoms. The **bond enthalpy** $D_{X–Y}$ of a diatomic molecule X—Y is the enthalpy change for the (usually hypothetical) process:

$$\mathrm{XY\,(g)} \rightarrow \mathrm{X\,(g) + Y\,(g)}$$

$$\Delta H^o(298K) = D_{x-y}$$

We have already used the term **bond energy** to describe this quantity, though strictly speaking the bond energy is a measure of ΔU rather than ΔH. As we have already seen, ΔU and ΔH are nearly equal, and so either term may be used.

As an example, let us consider the bond enthalpy for carbon monoxide. It is possible to establish the thermochemical equation

$$\mathrm{CO\,(g)} \rightarrow \mathrm{C\,(g) + O\,(g)}$$

$$\Delta H^o(298K) = 1073 kJ mol^{-1} \tag{10.9.1}$$

Accordingly we can write

$$\mathrm{C_{C\equiv O}} = 1073\,\mathrm{kJ\ mol^{-1}}$$

even though the process to which Eq. 10.9.1 corresponds is hypothetical: Neither carbon nor oxygen exists as a monatomic gas at 298 K. For triatomic and polyatomic molecules, the bond enthalpy is usually defined as a mean. In the case of water, for instance, we have

$$\mathrm{H_2O\,(g)} \rightarrow \mathrm{2\,H\,(g) + O\,(g)}$$

$$\Delta H^o(298K) = 927.2\mathrm{kJ\ mol^{-1}}$$

Since it requires 927.2 kJ to break open *two* O—H bonds, we take *half* this value as the mean bond enthalpy and write

$$D_{O-H} = 463.6\mathrm{kJ\ mol^{-1}}$$

In methanol, CH_3OH,however, a value of 427 kJ mol^{-1} for the O—H bond enthalpy fits the experimental data better. In other words the strength of the O—H varies somewhat from compound to compound. Because of this fact, we must expect to obtain only approximate results, accurate only to about ± 50 kJ mol^{-1}, from the use of bond enthalpies. Bond enthalpies for both single and multiple bonds are given in Table 10.9.1.

TABLE 10.9.1 Average Bond Energies/kJ mol^{-1}.

Table of Average Bond Energies (in kJ/mol)

Single Bonds

	I	Br	Cl	S	P	Si	F	O	N	C	H
H	299	366	431	347	322	323	566	467	391	416	436
C	213	285	327	272	264	301	486	336	285	356	
N	-	-	193	-	~200	355	272	201	160		
O	201	-	205	-	~340	368	190	146			
F	-	-	255	326	490	582	158				
Si	234	310	391	226	-	226					
P	184	264	319	-	209						
S	-	213	255	226							
Cl	209	217	242								
Br	180	193									
I	151										

Multiple Bonds

N = N	418	C = C	598
N ≡ N	946	C ≡ C	813
C = N	616	C = O (in CO_2, O=C=O)	803
C ≡ N	866	C = O (as in H_2C=O)	695
O = O (in O_2)	498	C ≡ O	1073

As an example of how a table of bond enthalpies can he used to predict the ΔH value for a reaction, let us take the simple case

$$\mathrm{H_2\,(g) + F_2\,(g)\ \rightarrow 2\,HF\,(g)} \tag{10.9.2}$$

298 K, 1 atm

We can regard this reaction as occurring in two stages (Figure 10.9.1). In the first stage all the reactant molecules are broken up into atoms:

$$\mathrm{H_2\,(g) + F_2\,(g)\ \rightarrow 2\,H\,(g) + F\,(g)} \tag{10.9.3}$$

298 K, 1 atm

For this stage

$$\Delta H_I = H_{H-H} + D_{F-F} \tag{10.9.4}$$

since 1 mol H_2 and 1 mol F_2 have been dissociated.

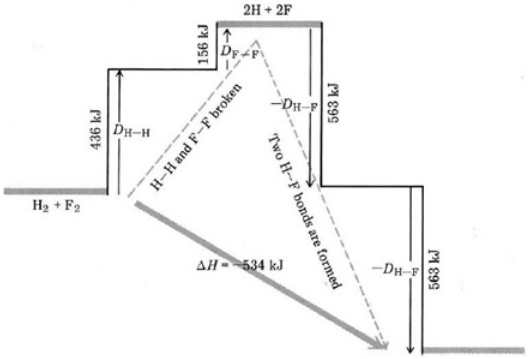


Figure 10.9.1 Bond-breaking-bond-making diagram for the reaction H_2 + F_2 + 2HF. When H_2 reacts with F_2, a strong H—H bond and a weak F—F bond are broken, while two extra-strong H—F bonds are made. The reaction is exothermic since more energy is released by the formation of the H—F bonds than is required to break the H—H and H—F bonds.

In the second stage the H and F atoms are reconstituted to form HF molecules:

$$\mathrm{2\,H\,(g) + 2\,F\,(g)\ \rightarrow 2\,HF\,(g)}$$

298 K, 1 atm

For which

$$\Delta H_{II} = -2D_{H-F}$$

where a negative sign is necessary since this stage corresponds to the *reverse* of dissociation.

Since Eq. 10.9.2 corresponds to the sum of Equations 10.9.3 and 10.9.4, Hess's law allows us to add Δ*H* values:

$$\Delta H^{o}_{reaction} = \Delta H_{I} + \Delta H_{II}$$

$$= D_{H-H} + D_{F-F} - 2DH - F$$

$$= (436 + 159 - 2 * 566)\text{kJ mol}^{-1}$$

$$= -539\text{kJ mol}^{-1}$$

We can work this same trick of subdividing a reaction into a bond-breaking stage followed by a bond-making stage for the general case of any gaseous reaction. In the first stage all the bonds joining the atoms in the reactant molecules are broken and a set of gaseous atoms results. For this stage

$$\Delta H_{I} = \sum_{\text{bonds broken}} D$$

The enthalpy change is the sum of the bond enthalpies for all bonds broken. In the second stage these gaseous atoms are reconstituted into the product molecules. For this second stage therefore

$$\Delta H_{II} = - \sum_{\text{bonds formed}} D$$

where the negative sign is necessary because the *reverse* of bond breaking is occurring in this stage. The total enthalpy change for the reaction at standard pressure is thus

$$\Delta H^{o} = \Delta H_{I} + \Delta H_{II}$$

or

$$\Delta H^{o} = \sum D(\text{bond broken}) - \sum D(\text{bond formed})$$

The use of this equation is illustrated in the next example.

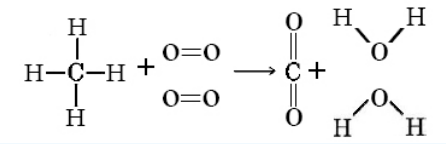
Example 10.9.1: Enthalpy Change

Using Table 10.9.1 calculate the value of Δ*H*°(298 K) for the reaction

$$\text{CH}_4\,(\text{g}) + 2\,\text{O}_2\,(\text{g}) \rightarrow \text{CO}_2\,(\text{g}) + 2\,\text{H}_2\text{O}\,(\text{g})$$

Solution

It is best to sketch the molecules and their bonds in order to make sure that none are missed.



Thus $\Delta H^{o} = \sum D(\text{bond broken}) - \sum D(\text{bond formed})$

\(= 4 D_{C\bond{-}H} + 2 D_{D\bond{=}D} - 2 D_{C\bond{=}O} - 4 D_{O\bond{-}H}\)

$$= (4 * 416 + 2 * 498 - 2 * 803 - 4 * 467)\text{kJ mol}^{-1}$$

$$= -814\text{kJ mol}^{-1}$$

The experimental value for this enthalpy change can be calculated from standard enthalpies of formation. It is –802.4 kJ mol^{-1}. The discrepancy is due to the unavoidable use of *mean* bond enthalpies in the calculation.

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10.10: Determining Enthalpies of Reaction from 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

$$\Delta H_{rxn} = \Delta H_f \tag{10.10.1}$$

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 10.10.1). Therefore, $O_2\,(g)$, $H_2\,(g)$, and graphite have ΔH_f^o values of zero.

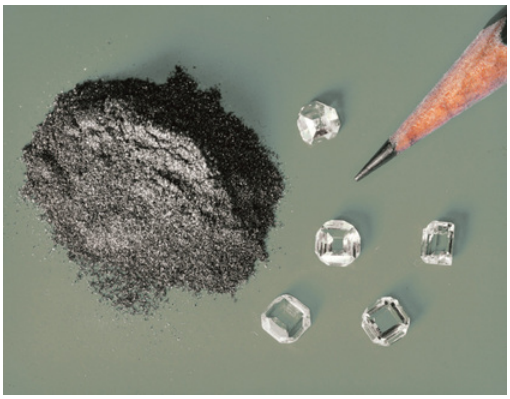


Figure 10.10.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ \tag{10.10.2}$$

It is not possible to measure the value of $\Delta H^o{}_{f}$ for glucose, −1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, O_2, and H_2 and measuring the heat evolved as glucose is formed since the reaction shown in Equation 10.10.2 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 $\Delta H^o{}_{f}$ 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 10.10.1: 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. $HCl\,(g)$
b. $MgCO_3\,(s)$
c. $CH_3(CH_2)_{14}CO_2H\,(s)$ (*palmitic acid*)

Given:

compound formula and phase.

Asked for:

balanced chemical equation for its formation from elements in standard states

Strategy:

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.

Solution:

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 $H_2\,(g)$ and $Cl_2\,(g)$, 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^o_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 10.10.1

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

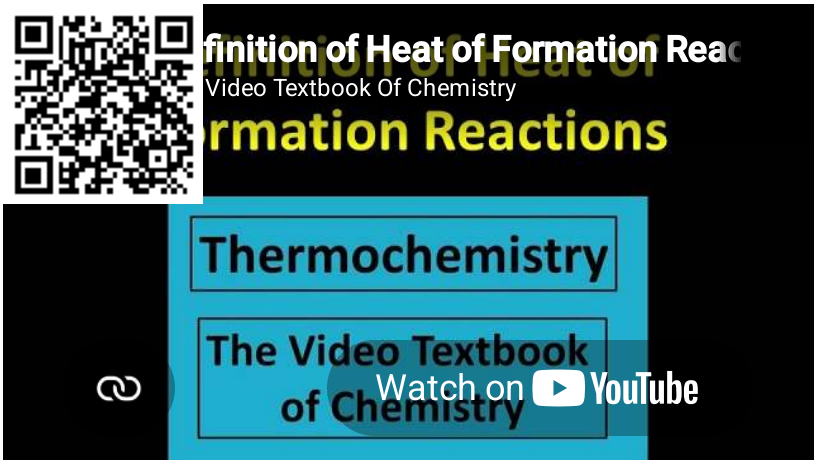
$$\mathrm{Na\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow NaCl\,(s)}$$

Answer b

$$\mathrm{H_2\,(g) + \tfrac{1}{8}\,S_8\,(s) + 2\,O_2\ (\ g) \rightarrow H_2\ SO_4(\ l)}$$

Answer c

$$\mathrm{2\,C\,(s) + O_2\,(g) + 2\,H_2\,(g) \longrightarrow CH_3CO_2H\,(l)}$$



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

$$aA + bB \rightarrow cC + dD \tag{10.10.3}$$

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:

$$\Delta H_{rxn}^o = \underbrace{\left[c\Delta H_f^o\left(C\right) + d\Delta H_f^o\left(D\right)\right]}_{\text{products}} - \underbrace{\left[a\Delta H_f^o\left(A\right) + b\Delta H_f^o\left(B\right)\right]}_{\text{reactants}} \tag{10.10.4}$$

More generally, we can write

$$\Delta H_{rxn}^o = \sum m\Delta H_f^o\left(products\right) - \sum n\Delta H_f^o\left(reactants\right) \tag{10.10.5}$$

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 10.10.5 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^o values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$\mathrm{C_6H_{12}O_6\,(s) + 6\,O_2\,(g)\ \rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l)} \tag{10.10.6}$$

Using Equation 10.10.5, we write

$$\begin{aligned}\Delta H_f^o = &\left\{6\Delta H_f^o\left[CO_2\left(g\right)\right] + 6\Delta H_f^o\left[H_2O\left(g\right)\right]\right\} \\ &- \left\{\Delta H_f^o\left[C_6H_{12}O_6\left(s\right)\right] + 6\Delta H_f^o\left[O_2\left(g\right)\right]\right\}\end{aligned} \tag{10.10.7}$$

From Table T1, the relevant ΔH^o_f values are $\Delta H^o_f\,[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f\,[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f\,[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^o_f\,[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 10.10.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\Delta H_{comb}^o = \left[6\left(-393.5\ kJ/mol\right) + 6\left(-285.8\ kJ/mol\right)\right] - \left[-1273.3 + 6\left(0\ kJ\ mol\right)\right] \tag{10.10.8}$$

$$= -2802.5\ kJ/mol \tag{10.10.9}$$

As illustrated in Figure 10.10.2, we can use Equation 10.10.8 to calculate ΔH_f^o 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_{comb}^o. 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_f^o values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}\Delta H_1^o &= \Delta H_f^o\,[glucose\,(s)] \\ &= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) \\ &= +1273.3\ kJ \\ \Delta H_2^o &= 6\Delta H_f^o\,[O_2\,(g)] \\ &= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) \\ &= 0\ kJ\end{aligned} \tag{10.10.10}$$

> *Recall that when we reverse a reaction, we must also reverse the* ***sign*** *of the accompanying enthalpy change (Equation* 10.10.4 *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.

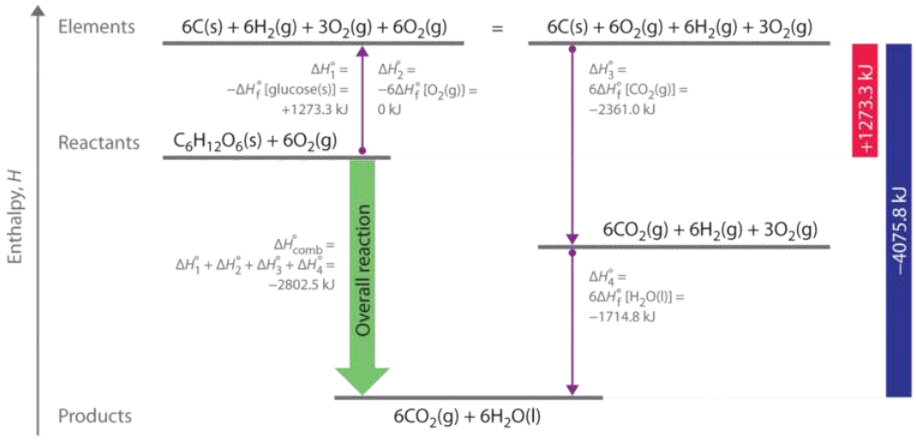


Figure 10.10.1: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the 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 10.10.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\begin{aligned}\Delta H_3^o &= \Delta H_f^o\,[CO_2\,(g)] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ \\ \Delta H_4^o &= 6\Delta H_f^o\,[H_2O\,(l)] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ\end{aligned} \tag{10.10.11}$$

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):

$$\Delta H^o_{comb} = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{10.10.12}$$

This is the same result we obtained using the “products minus reactants” rule (Equation 10.10.5) and ΔH^o_f values. The two results must be the same because Equation 10.10.12 is just a more compact way of describing the thermochemical cycle shown in Figure

10.10.1.

Example 10.10.2: 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^o_{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^o_{comb} per mole and per gram

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 10.10.5 and the values from Table T1 to calculate ΔH^o_{comb} 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 10.10.8 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 10.10.5 (“products minus reactants”) with ΔH^o_f values from Table T1 (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned}\Delta H^o_{comb} &= \sum m\Delta H_f^o\,(products) - \sum n\Delta H_f^o\,(reactants)\\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\,)]\\ &\quad - [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\,)]\\ &= -9977.3\ kJ/mol\end{aligned}$$

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 10.10.8, \(ΔH^o_f\) 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 10.10.2: 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):

$$\mathrm{CO\ (\ g\ ) + H_2O\ (g\ ) \longrightarrow CO_2\,(g) + H_2\ (\ g\ )}$$

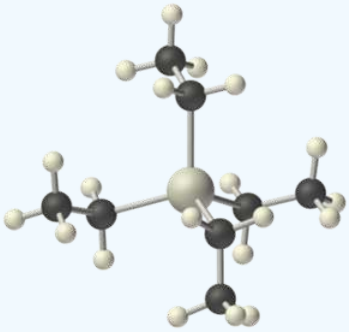
Answer

−41.2 kJ/mol

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_f^o which we cannot obtain otherwise. This procedure is illustrated in Example 10.10.3.

Example 10.10.3: 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 $CO_2\,(g)$, $H_2O\,(l)$, and red $PbO\,(s)$. What is the standard enthalpy of formation of tetraethyllead, given that ΔH_f^o is −19.29 kJ/g for the combustion of tetraethyllead and ΔH_f^o of red PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH_{comb}^o 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 10.10.5 to get the equation for ΔH^o_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:

$$2\,(C_2H_5)_4Pb\,(l) + 27\,O_2\,(g) \longrightarrow 2\,PbO\,(s) + 16\,CO_2\,(g) + 20\,H_2O\,(l)$$

Using Equation 10.10.5 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 $\Delta H_f^o[(C_2H_5)_4Pb]$ 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 $\Delta H_f^o[(C_2H_5)_4Pb]$ 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:

$$\Delta H^o_{comb} = \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right)$$
$$= -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH^o_{rxn} is

$$\Delta H^o_{rxn} = 2\ \cancel{mol\ (C_2H5)_4\ Pb}\left(\frac{-6329\ kJ}{1\ \cancel{mol\ (C_2H5)_4\ Pb}}\right)$$
$$= -12,480\ kJ$$

C Inserting the appropriate values into the equation for $\Delta H^o_f[(C_2H_5)_4Pb]$ gives

$$\Delta H^o_f[(C_2H_4)_4 Pb] = [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] + [10\ mol\ H_2O \times (-285.8\ kJ/mol)] + [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2]\ [12,480.2\ kJ/mol\ (C_2H_5)_4\ Pb]$$
$$= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol$$

Exercise 10.10.3

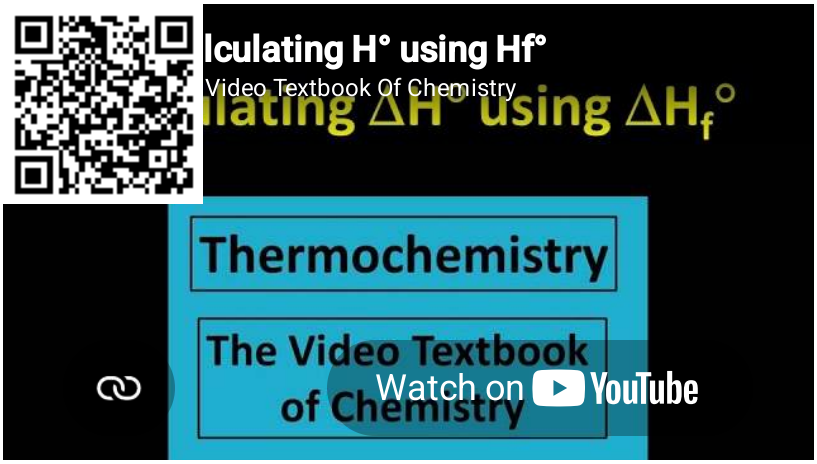
Ammonium sulfate, $(NH_4)_2SO_4$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$2\,NH_3\,(g) + H_2SO_4\,(aq) \rightarrow (NH_4)_2SO_4\,(s)$$

The value of ΔH^o_{rxn} is -179.4 kJ/mole H_2SO_4. Use the data in Table T1 to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer

−1181 kJ/mol



Calculating DH° using DHf°: https://youtu.be/Y3aJJno9W2c

Summary

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 ºC 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^o_f) 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^o_{rxn}) 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

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10.11: Lattice Energy

Discussion Questions

- How is lattice energy estimated using Born-Haber cycle?
- How is lattice energy related to crystal structure?

The Lattice energy, U, is the amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions.

$$\mathrm{M}_a\ \mathrm{L}_b\,(\mathrm{s})\ \rightarrow a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g}) \tag{10.11.1}$$

This quantity cannot be experimentally determined directly, but it can be estimated using a Hess Law approach in the form of *Born-Haber cycle*. It can also be calculated from the electrostatic consideration of its crystal structure. As defined in Equation 10.11.1, the lattice energy is positive, because energy is always required to separate the ions. For the reverse process of Equation 10.11.1:

$$a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g})\ \rightarrow \mathrm{M}_a\mathrm{L}_b\,(\mathrm{s}) \tag{10.11.2}$$

the energy released is called **energy of crystallization** (E_{cryst}). Therefore,

$$U_{lattice} = -E_{cryst} \tag{10.11.3}$$

Values of lattice energies for various solids have been given in literature, especially for some common solids. Some are given here.

Table 10.11.1: Comparison of Lattice Energies (U in kJ/mol) of Some Salts

Solid	*U*	Solid	*U*	Solid	*U*	Solid	*U*
LiF	1036	LiCl	853	LiBr	807	LiI	757
NaF	923	NaCl	786	NaBr	747	NaI	704
KF	821	KCl	715	KBr	682	KI	649
MgF_2	2957	$MgCl_2$	2526	$MgBr_2$	2440	MgI_2	2327

The following trends are obvious at a glance of the data in Table 10.11.1:

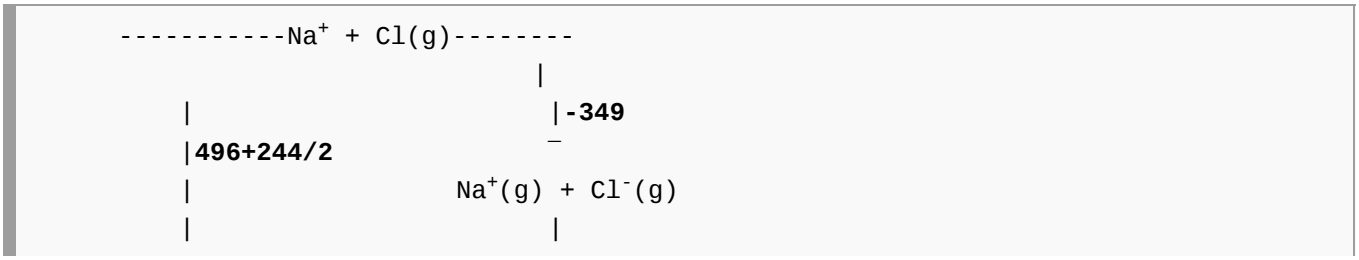
- As the ionic radii of either the cation or anion increase, the lattice energies decrease.
- The solids consists of divalent ions have much larger lattice energies than solids with monovalent ions.

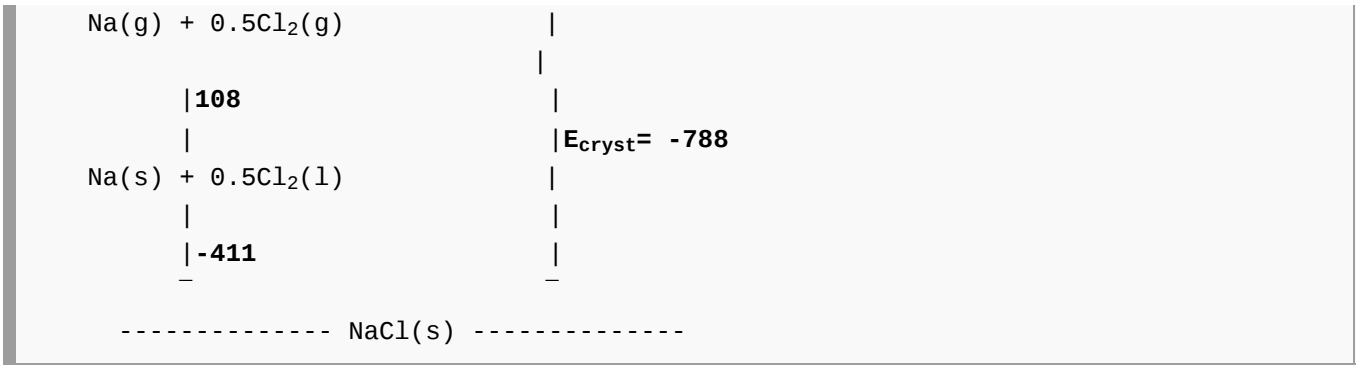
How is lattice energy estimated using Born-Haber cycle?

Estimating lattice energy using the Born-Haber cycle has been discussed in Ionic Solids. For a quick review, the following is an example that illustrate the estimate of the energy of crystallization of NaCl.

Hsub of Na = 108 kJ/mol (Heat of sublimation)
D of Cl2 = 244 (Bond dissociation energy)
IP of Na(g) = 496 (Ionization potential or energy)
EA of Cl(g) = -349 (Electron affinity of Cl)
Hf of NaCl = -411 (Enthalpy of formation)

The Born-Haber cycle to evaluate $E_{lattice}$ is shown below:





E_{cryst} = -411-(108+496+244/2)-(-349) kJ/mol
= -788 kJ/mol.

Discussion

The value calculated for U depends on the data used. Data from various sources differ slightly, and so is the result. The lattice energies for NaCl most often quoted in other texts is about 765 kJ/mol.

Compare with the method shown below

Na(s) + 0.5 Cl_2(l) ® NaCl(s)	- 411	H_f
Na(g) ® Na(s)	- 108	-H_{sub}
Na^+(g) + e ® Na(g)	- 496	-*IP*
Cl(g) ® 0.5 Cl_2(g)	- 0.5 * 244	-0.5*D
Cl^-(g) ® Cl(g) + 2 e	349	-*EA*
Add all the above equations leading to		
Na^+(g) + Cl^-(g) ® NaCl(s)	-788 kJ/mol = E_{cryst}	

Lattice Energy is Related to Crystal Structure

There are many other factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulson from ions of opposite charge and ions of the same charge.

As an example, let us consider the the NaCl crystal. In the following discussion, assume r be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are 6 Cl^- ions at a distance 1r, 12 Na^+ ions at a distance 2r, 8 Cl^- at 3r, 6 Na^+ at 4r, 24 Na^+ at 5r, and so on. Thus, the energy due to one ion is

$$E = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{10.11.4}$$

The Madelung constant, M, is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \tag{10.11.5}$$

with

- Z is the number of charges of the ions, (e.g., 1 for NaCl),
- e is the charge of an electron ($1.6022 \times 10^{-19}\ C$),
- $4\pi\epsilon_o$ is 1.11265x10^{-10} C^2/(J m).

The above discussion is valid only for the sodium chloride (also called rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for several structural types are given in Table 6.13.1.

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Table 10.11.2: Madelung Constants

Compound	Crystal Lattice	M	A : C	Type
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
CaF_2	Cubic	2.51939	8 : 4	Fluorite
$CdCl_2$	Hexagonal	2.244		
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132		
TiO_2 (rutile)	Tetragonal	2.408	6 : 3	Rutile
$bSiO_2$	Hexagonal	2.2197		
Al_2O_3	Rhombohedral	4.1719	6 : 4	Corundum
A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.				

Madelung constants for a few more types of crystal structures are available from the Handbook Menu. There are other factors to consider for the evaluation of energy of crystallization, and the treatment by *M. Born* led to the formula for the evaluation of crystallization energy E_{cryst}, for a mole of **crystalline solid**.

$$E_{cryst} = \frac{NZ^2e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{10.11.6}$$

where *N* is the Avogadro's number (6.022x10^{-23}), and *n* is a number related to the electronic configurations of the ions involved. The *n* values and the electronic configurations (e.c.) of the corresponding inert gases are given below:

n =	5	7	9	10	12
e.c.	He	Ne	Ar	Kr	Xe

The following values of *n* have been suggested for some common solids:

n =	5.9	8.0	8.7	9.1	9.5
e.c.	LiF	LiCl	LiBr	NaCl	NaBr

Example 10.11.1

Estimate the energy of crystallization for NaCl.

Solution

Using the values giving in the discussion above, the estimation is given by Equation 10.11.6:

$$E_c ryst = \frac{(6.022 \times 10^{23}/mol(1.6022 \times 10^{-19})^2(1.747558)}{4\pi\,(8.854 \times 10^{-12}C^2/m)(282 \times 10^{-12}\,m}\left(1 - \frac{1}{9.1}\right)$$
$$= -766kJ/mol$$

Discussion

Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Haber cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

Exercise 10.11.1

Which one of the following has the largest lattice energy? LiF, NaF, CaF_2, AlF_3

Answer

Skill: Explain the trend of lattice energy.

Exercise 10.11.2

Which one of the following has the largest lattice energy? LiCl, NaCl, $CaCl_2$, Al_2O_3

Answer

Corrundum Al_2O_3 has some covalent character in the solid as well as the higher charge of the ions.

Exercise 10.11.3

Lime, CaO, is know to have the same structure as NaCl and the edge length of the unit cell for CaO is 481 pm. Thus, Ca-O distance is 241 pm. Evaluate the energy of crystallization, E_{cryst} for CaO.

Answer

Energy of crystallization is -3527 kJ/mol

Skill: Evaluate the lattice energy and know what values are needed.

Exercise 10.11.4

Assume the interionic distance for $NaCl_2$ to be the same as those of NaCl (r = 282 pm), and assume the structure to be of the fluorite type (M = 2.512). Evaluate the energy of crystallization, E_{cryst} .

Answer

-515 kJ/mol

Discussion: This number has not been checked. If you get a different value, please let me know.

Contributors and Attributions

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CHAPTER OVERVIEW

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11.1: Supersonic Skydiving and the Risk of Decompression



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11.2: Pressure- The Result of Particle Collisions

Learning Objectives

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure 11.2.1). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

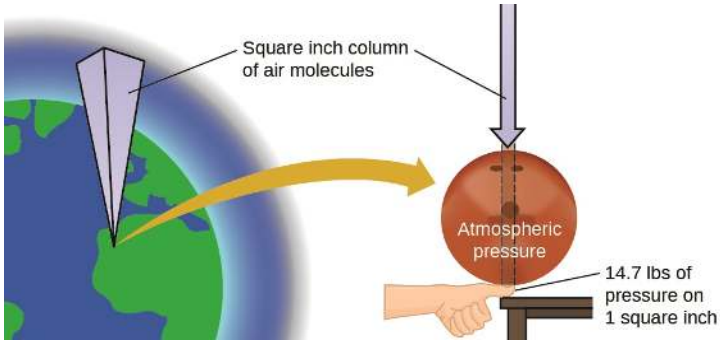


Figure 11.2.1: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

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

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



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.

Pressure is defined as the force exerted on a given area:

$$P = \frac{F}{A} \tag{11.2.1}$$

Since pressure is directly proportional to force and inversely proportional to area (Equation 11.2.1), pressure can be increased either by either **increasing** the amount of force or by **decreasing** the area over which it is applied. Correspondingly, pressure can be decreased by either **decreasing** the force or **increasing** the area.

Let's apply the definition of pressure (Equation 11.2.1) to determine which would be more likely to fall through thin ice in Figure 11.2.2.—the elephant or the figure skater?



Figure 11.2.2: Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi).

Figure a is a photo of a large gray elephant on grassy, beige terrain. Figure b is a photo of a figure skater with her right skate on the ice, upper torso lowered, arms extended upward behind her chest, and left leg extended upward behind her.

A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

$$\text{pressure per elephant foot} = 14,000 \frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2 \tag{11.2.2}$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2 \tag{11.2.3}$$

Even though the elephant is more than one hundred times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall through thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2 \tag{11.2.4}$$

The SI unit of pressure is the pascal (Pa), with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or bar (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—pounds per square inch (psi)—for example, in car tires. Pressure can also be measured using the unit atmosphere (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 11.2.1 provides some information on these and a few other common units for pressure measurements

Table 11.2.1: Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
pascal (Pa)	1 Pa = 1 N/m^2	recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa	
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi	
atmosphere (atm)	1 atm = 101,325 Pa	air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly)	commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar	
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa	used by aviation industry, also some weather reports
torr	$1\ \text{torr} = \frac{1}{760}\ \text{atm}$	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr	

Example 11.2.1: Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 9.2.1.

a. $29.2\ \cancel{\text{in Hg}} \times \frac{25.4\ \cancel{\text{mm}}}{1\ \cancel{\text{in}}} \times \frac{1\ \text{torr}}{1\ \cancel{\text{mm Hg}}} = 742\ \text{torr}$

b. $742\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.976\ \text{atm}$

c. $742\ \cancel{\text{torr}} \times \frac{101.325\ \text{kPa}}{760\ \cancel{\text{torr}}} = 98.9\ \text{kPa}$

d. $98.9\ \cancel{\text{kPa}} \times \frac{1000\ \cancel{\text{Pa}}}{1\ \cancel{\text{kPa}}} \times \frac{1\ \cancel{\text{bar}}}{100,000\ \cancel{\text{Pa}}} \times \frac{1000\ \text{mbar}}{1\ \cancel{\text{bar}}} = 989\ \text{mbar}$

Exercise 11.2.1

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a barometer (Figure 11.2.3). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts

pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

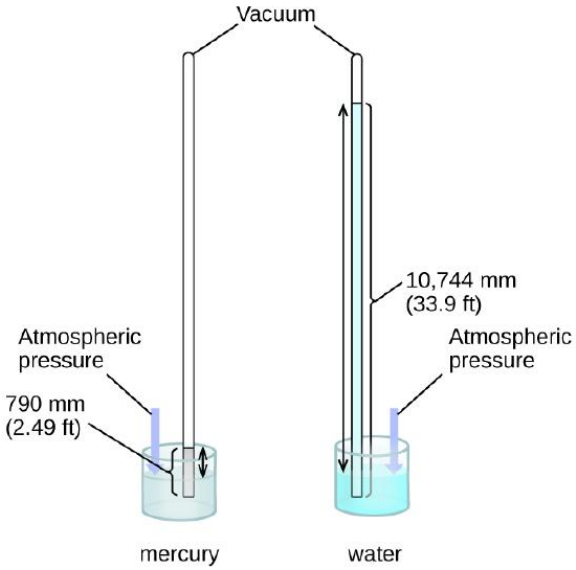


Figure 11.2.3: In a barometer, the height, h, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

Two barometers are in vacuum. One utilizes mercury while the other uses water in the capillary tube. Both barometers are exposed to atmospheric pressure. The barometer with mercury shows mercury levels of 2.49 feet. The barometer with water has a much greater level of 33.9 feet.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The torr was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as hydrostatic pressure, *p*:

$$p = h\rho g \tag{11.2.5}$$

where

- h is the height of the fluid,
- ρ is the density of the fluid, and
- g is acceleration due to gravity.

Example 11.2.2: Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = $13.6\ g/cm^3$.

Solution

The hydrostatic pressure is given by Equation 11.2.5, with $h = 760\ mm$, $\rho = 13.6\ g/cm^3$, and $g = 9.81\ m/s^2$. Plugging these values into the Equation 11.2.5 and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

$$101,325\ N/\mathrm{m}^2 = 101,325\ \frac{\mathrm{kg}\cdot\mathrm{m/s}^2}{\mathrm{m}^2} = 101,325\ \frac{\mathrm{kg}}{\mathrm{m}\cdot\mathrm{s}^2}$$

$$p = \left(760\ \text{mm} \times \frac{1\ \text{m}}{1000\ \text{mm}}\right) \times \left(\frac{13.6\ \text{g}}{1\ \text{cm}^3} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{(100\ \text{cm})^3}{(1\ \text{m})^3}\right) \times \left(\frac{9.81\ \text{m}}{1\ \text{s}^2}\right)$$
$$= (0.760\ \text{m})(13,600\ \text{kg/m}^3)(9.81\ \text{m/s}^2) = 1.01 \times 10^5\ \text{kg/ms}^2 = 1.01 \times 10^5 N/\text{m}^2$$
$$= 1.01 \times 10^5\ \text{Pa}$$

Exercise 11.2.2

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3.

Answer

10.3 m

A manometer is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (*h* in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure 11.2.3) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

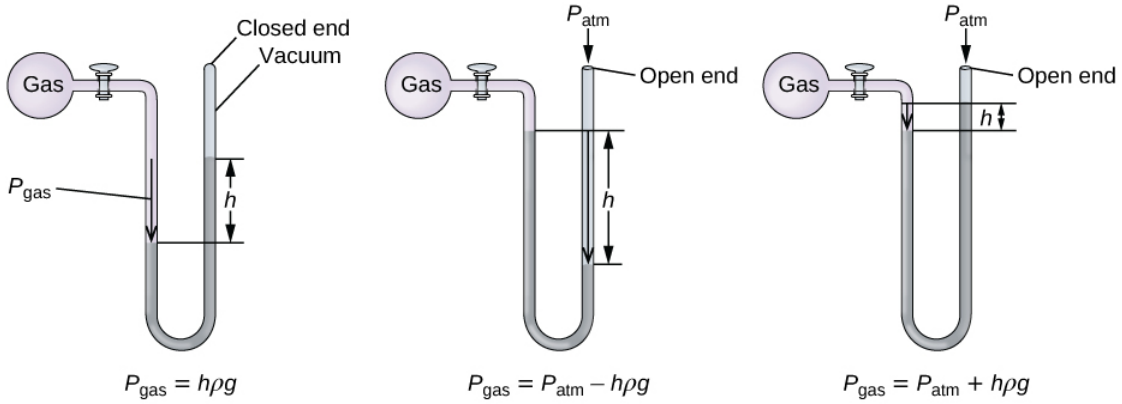


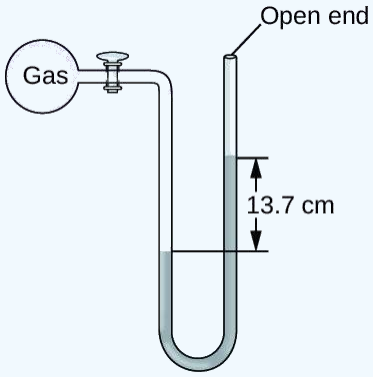
Figure 11.2.4: A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density.

The first manometer is closed end. The gas in the bulb exerts a certain pressure on the liquid in the tube so that the height, h, between the two levels of liquid on both sides of the U tube is proportional to the pressure. The equation is P subscript gas equals to h rho g. The second manometer has an open end. The equation for P subscript gas is equals to P subscript atm minus h rho g. The final manometer is also open ended and has equation of P subscript gas equals to P subscript atm plus h rho g for cases where pressure of the gas is greater than atmospheric pressure.

Example 11.2.3: Calculation of Pressure Using an Open-End Manometer

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown below. Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 13.7 centimeters. The level on the right side is higher than the left.

Solution

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

a. In mm Hg, this is: 137 mm Hg + 760 mm Hg = 897 mm Hg

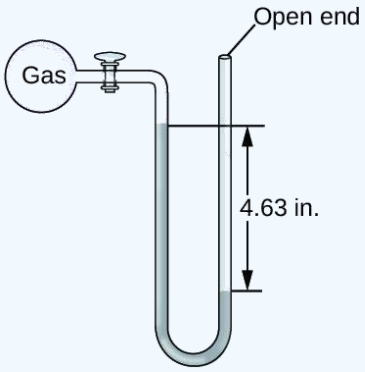
b. $897\ \cancel{\text{mmHg}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 1.18\ \text{atm}$

c. $1.18\ \cancel{\text{atm}} \times \dfrac{101.325\ \text{kPa}}{1\ \cancel{\text{atm}}} = 1.20 \times 10^2\ \text{kPa}$

Exercise 11.2.3

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown below Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 4.63 inches. The level on the left side is higher than the right.

Answer a

642 mm Hg

Answer b

0.845 atm

Answer c

85.6 kPa

Application: Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = “pulse”). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure 11.2.5). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff’s pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart’s ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).



Figure 11.2.5: (a) A medical technician prepares to measure a patient’s blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth’s weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure 11.2.5) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

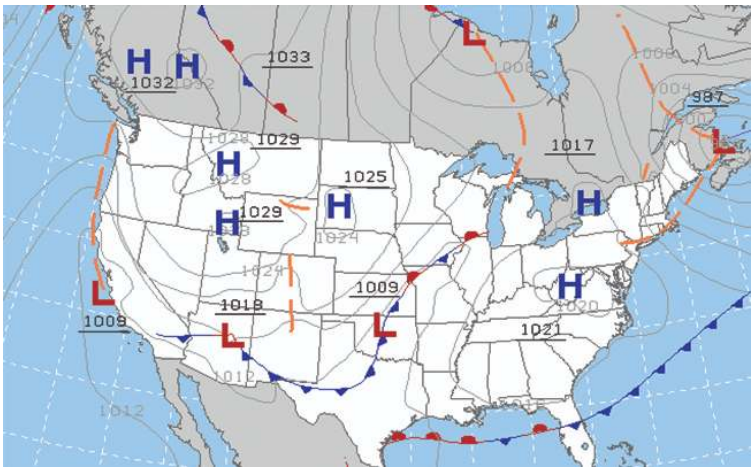


Figure 11.2.6: Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)

A weather map of the United States is shown which points out areas of high and low pressure with the letters H in blue and L in red. There are curved grey lines throughout the United States region as well as beyond it around area of Canada and the oceans.

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure 11.2.7: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

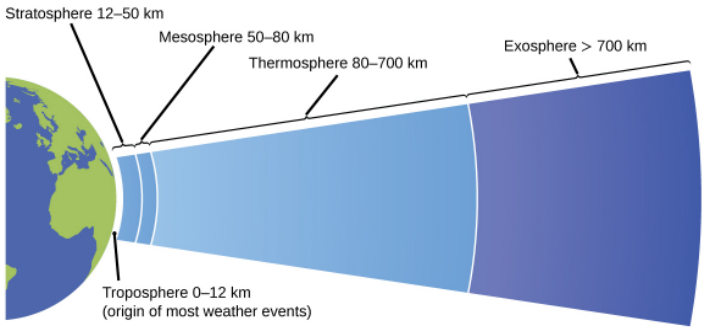


Figure 11.2.7: Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

The different layers of the atmosphere is illustrated as a cross sectional slice of the Earth's atmosphere. The different thickness of each layer is shown. The thermosphere has the largest portion, followed by the exosphere, stratosphere, mesosphere, and troposphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas

pressures can be measured using one of several types of manometers.

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Glossary

atmosphere (atm)
unit of pressure; 1 atm = 101,325 Pa

bar
(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer
device used to measure atmospheric pressure

hydrostatic pressure
pressure exerted by a fluid due to gravity

manometer
device used to measure the pressure of a gas trapped in a container

pascal (Pa)
SI unit of pressure; 1 Pa = 1 N/m^2

pounds per square inch (psi)
unit of pressure common in the US

pressure
force exerted per unit area

torr
unit of pressure; $1 \text{ torr} = \frac{1}{760} \text{ atm}$

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11.3: The Simple Gas Laws- Boyle's Law, Charles's Law and Avogadro's Law

Learning Objectives

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

Early scientists explored the relationships among the pressure of a gas (P) and its temperature (T), volume (V), and amount (n) by holding two of the four variables constant (amount and temperature, for example), varying a third (such as pressure), and measuring the effect of the change on the fourth (in this case, volume). The history of their discoveries provides several excellent examples of the scientific method.

The Relationship between Pressure and Volume: Boyle's Law

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

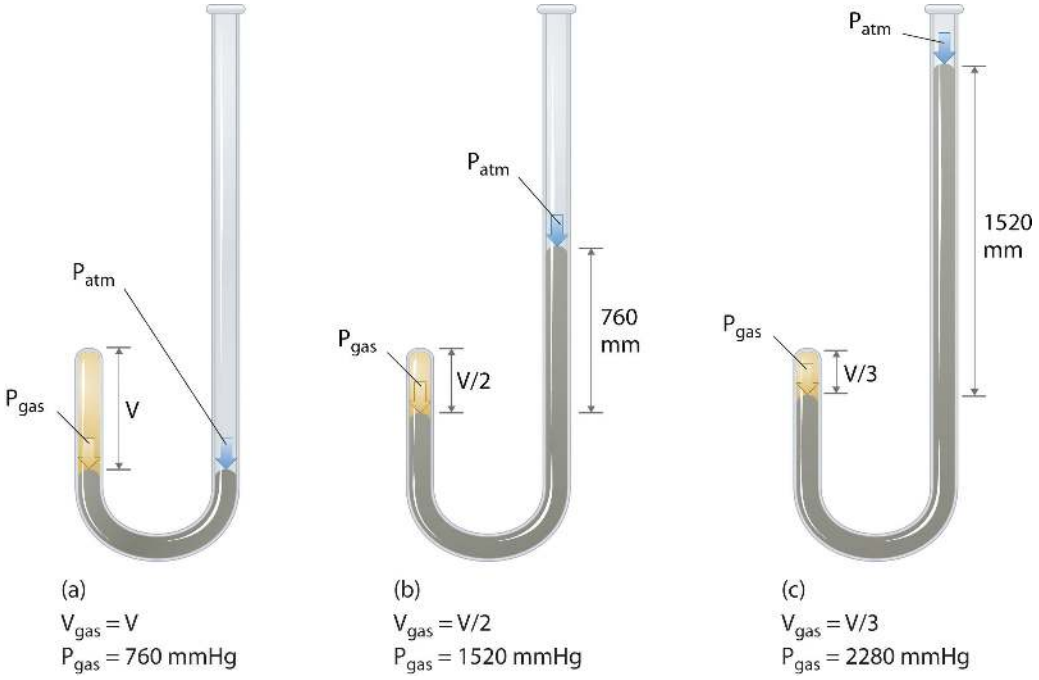


Figure 11.3.1: Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume. (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V. (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is $V/2$. (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to $V/3$ (CC BY-SA-NC; anonymous).

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure 11.3.1. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure plus the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure 11.3.2). A simple plot of V versus P gives a curve called a hyperbola and reveals an inverse relationship between pressure

and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

$$PV = \text{constant} \tag{11.3.1}$$

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

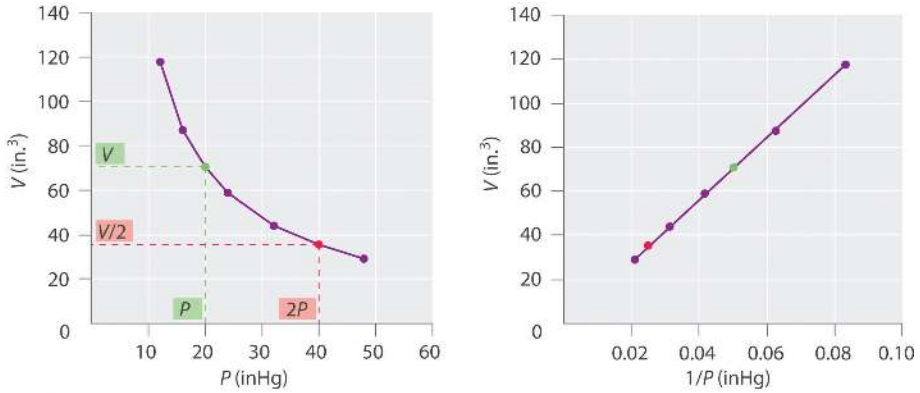
$$V = \frac{\text{const.}}{P} = \text{const.}\left(\frac{1}{P}\right) \tag{11.3.2}$$

or

$$V \propto \frac{1}{P} \tag{11.3.3}$$

where the ∝ symbol is read "is proportional to." A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equations 11.3.1 and 11.3.3. Dividing both sides of Equation 11.3.1 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle's law, after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.* This law in practice is shown in Figure 11.3.2.

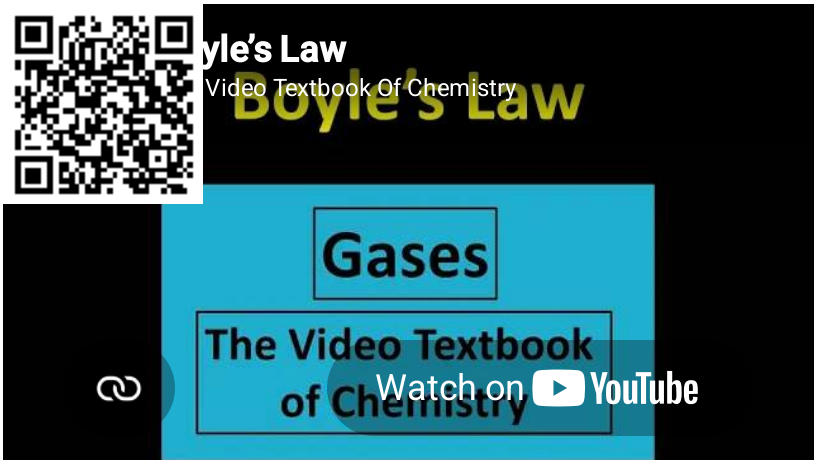
P (inHg)	*V* (in.^{3})	*PV*
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400



(a) Data from Boyle's experiment **(b) Volume vs. pressure** **(c) Volume vs. 1/pressure**

Figure 11.3.2: Plots of Boyle's Data. (a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.^{3} rather than cm^3) and the pressure (in. Hg rather than mmHg). (b) This plot of pressure versus volume is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation V = constant/P (CC BY-SA-NC; anonymous).

> *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure*



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 11.3.3).A sample of gas cannot really have a volume of zero because any sample of matter must have some volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above −273.15°C. Note from part (a) in Figure 11.3.3 that the slope of the plot of V versus T varies for the same gas at different pressures but that the intercept remains constant at −273.15°C. Similarly, as shown in part (b) in Figure 11.3.3, plots of V versus T for different amounts of varied gases are straight lines with different slopes but the same intercept on the T axis.

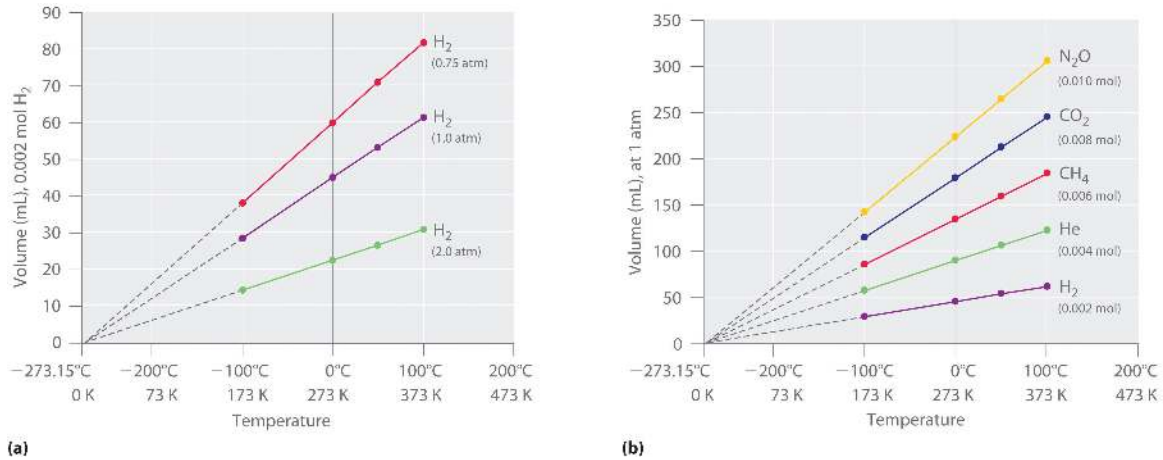


Figure 11.3.3: The Relationship between Volume and Temperature. (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to $V = 0$. The temperature scale is given in both degrees Celsius and kelvins. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at $V = 0$ (−273.15°C = 0 K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of $V = 0$ at −273.15°C, regardless of the identity or the amount of the gas (CC BY-SA-NC; anonymous).

The significance of the invariant T intercept in plots of V versus T was recognized in 1848 by the British physicist William Thomson (1824–1907), later named Lord Kelvin. He postulated that −273.15°C was the lowest possible temperature that could theoretically be achieved, for which he coined the term absolute zero (0 K).

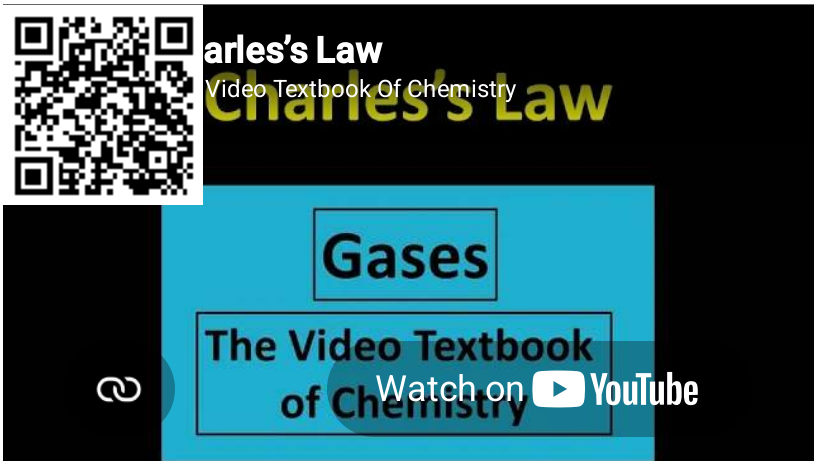
We can state Charles's and Gay-Lussac's findings in simple terms: At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins). This relationship, illustrated in part (b) in Figure 11.3.3 is often referred to as Charles's law and is stated mathematically as

$$V = \text{const.}\ T \tag{11.3.4}$$

or

$$V \propto T \tag{11.3.5}$$

with *temperature expressed in kelvins*, not *in degrees Celsius*. Charles's law is valid for virtually all gases at temperatures well above their boiling points.



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 11.3.4). This is the historic "Avogadro's hypothesis."

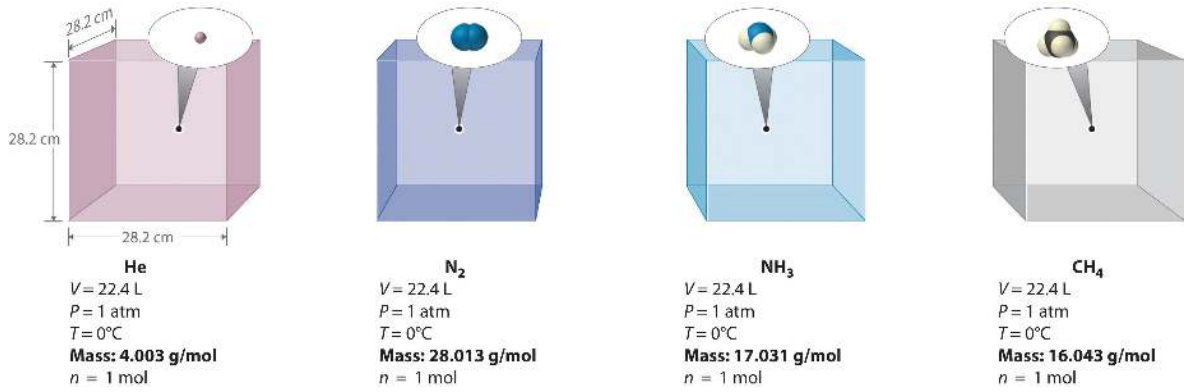


Figure 11.3.4: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

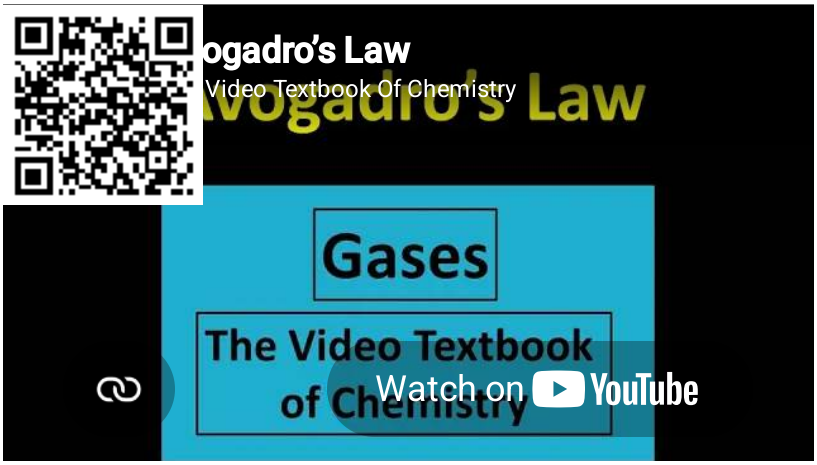
A logical corollary to Avogadro's hypothesis (sometimes called Avogadro's law) describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = \text{const.}\ (n) \tag{11.3.6}$$

or

$$V \propto .n@\ \text{constant T and P} \tag{11.3.7}$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.



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 11.3.5. Volume *increases* with increasing temperature or amount, but *decreases* with increasing pressure.

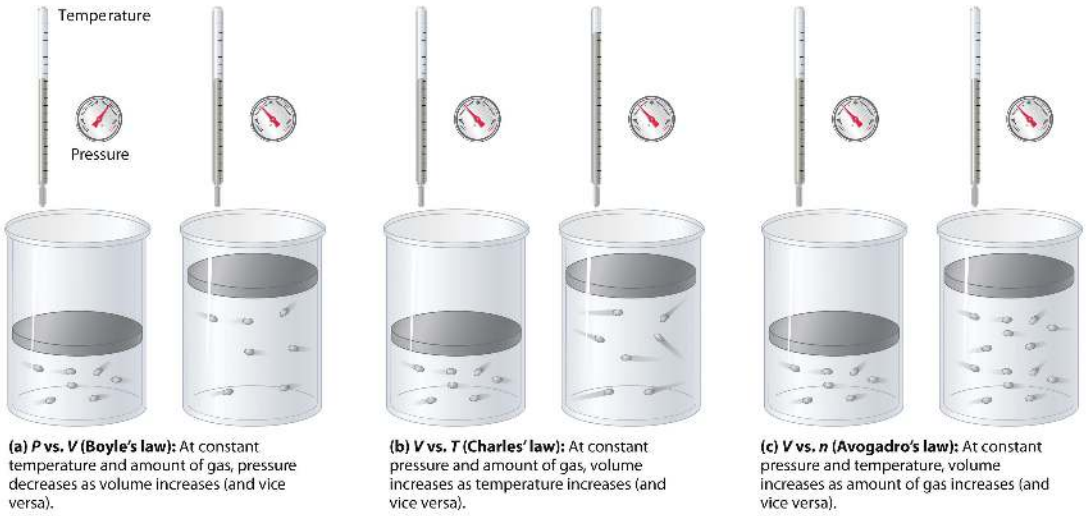


Figure 11.3.5: The Empirically Determined Relationships among Pressure, Volume, Temperature, and Amount of a Gas. The thermometer and pressure gauge indicate the temperature and the pressure qualitatively, the level in the flask indicates the volume, and the number of particles in each flask indicates relative amounts (CC BY-SA-NC; anonymous).

Summary

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle's law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles's law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro's law**). Plots of the volume of gases versus temperature extrapolate to zero volume at −273.15°C, which is **absolute zero (0 K)**, the lowest temperature possible. Charles's law implies that the volume of a gas is directly proportional to its absolute temperature.

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11.4: The Ideal Gas Law

Learning Objectives

- Derive the ideal gas law from the constituent gas laws
- To use the ideal gas law to describe the behavior of a gas.

In this module, the relationship between pressure, temperature, volume, and amount of a gas are described and how these relationships can be combined to give a general expression that describes the behavior of a gas.

Deriving the Ideal Gas Law

Any set of relationships between a single quantity (such as V) and several other variables (P, T, and n) can be combined into a single expression that describes all the relationships simultaneously. The three individual expressions were derived previously:

- **Boyle's law**

$$V \propto \frac{1}{P} \text{ @ constant n and T}$$

- **Charles's law**

$$V \propto T \text{ @ constant n and P}$$

- **Avogadro's law**

$$V \propto n \text{ @ constant T and P}$$

Combining these three expressions gives

$$V \propto \frac{nT}{P} \tag{11.4.1}$$

which shows that the volume of a gas is proportional to the number of moles and the temperature and inversely proportional to the pressure. This expression can also be written as

$$V = \text{Cons.} \left(\frac{nT}{P}\right) \tag{11.4.2}$$

By convention, the proportionality constant in Equation 11.4.1 is called the gas constant, which is represented by the letter R. Inserting R into Equation 11.4.2 gives

$$V = \frac{RnT}{P} = \frac{nRT}{P} \tag{11.4.3}$$

Clearing the fractions by multiplying both sides of Equation 11.4.4 by P gives

$$PV = nRT \tag{11.4.4}$$

This equation is known as the **ideal gas law**.

An ideal gas is defined as a hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces and can be completely described by the ideal gas law. In reality, there is no such thing as an ideal gas, but an ideal gas is a useful conceptual model that allows us to understand how gases respond to changing conditions. As we shall see, under many conditions, most real gases exhibit behavior that closely approximates that of an ideal gas. The ideal gas law can therefore be used to predict the behavior of real gases under most conditions. The ideal gas law does not work well at very low temperatures or very high pressures, where deviations from ideal behavior are most commonly observed.

> *Significant deviations from ideal gas behavior commonly occur at low temperatures and very high pressures.*

Before we can use the ideal gas law, however, we need to know the value of the gas constant R. Its form depends on the units used for the other quantities in the expression. If V is expressed in liters (L), P in atmospheres (atm), T in kelvins (K), and n in moles (mol), then

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \tag{11.4.5}$$

Because the product PV has the units of energy, R can also have units of J/(K•mol):

$$R = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{11.4.6}$$

Standard Conditions of Temperature and Pressure

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and $1 \text{ bar} = 100 \text{ kPa} = 10^5 \text{ Pa}$ pressure, referred to as standard temperature and pressure (**STP**).

$$\text{STP:} \qquad T = 273.15 \text{ K and } P = 1 \text{ bar} = 10^5 \text{ Pa}$$

Please note that STP was defined differently in the past. The old definition was based on a standard pressure of 1 atm.

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 11.4.4:

$$V = \frac{nRT}{P} \tag{11.4.7}$$

Thus the volume of 1 mol of an ideal gas is **22.71 L at STP** and **22.41 L at 0°C and 1 atm**, approximately equivalent to the volume of three basketballs. The molar volumes of several real gases at 0°C and 1 atm are given in Table 10.3, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at 0°C and 1 atm. The relationships described in Section 10.3 as Boyle's, Charles's, and Avogadro's laws are simply special cases of the ideal gas law in which two of the four parameters (P, V, T, and n) are held fixed.

Table 11.4.1: Molar Volumes of Selected Gases at 0°C and 1 atm

Gas	Molar Volume (L)
He	22.434
Ar	22.397
H_2	22.433
N_2	22.402
O_2	22.397
CO_2	22.260
NH_3	22.079

Applying the Ideal Gas Law

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

Example 11.4.1

The balloon that Charles used for his initial flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft^3), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: amount of gas

Strategy:

A. Solve the ideal gas law for the unknown quantity, in this case *n*.

B. Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 11.4.4) for n, we obtain

$$745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.980 \text{ atm}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.08206 (L•atm)/(K•mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$T = 273 + 30 = 303\text{K}$$

Substituting these values into the expression we derived for *n*, we obtain

$$\begin{aligned} n &= \frac{PV}{RT} \\ &= \frac{0.980 \text{ atm} \times 31150 \text{ L}}{0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 303 \text{ K}} \\ &= 1.23 \times 10^3 \ mol \end{aligned}$$

Exercise 11.4.1

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25°C?

Answer

1.5 atm

In Example 11.4.1, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 11.4.5.

General Gas Equation

When a gas is described under two different conditions, the ideal gas equation must be applied twice - to an initial condition and a final condition. This is:

$$\begin{array}{ll} \text{Initial condition } (i) & \text{Final condition} (f) \\ P_i V_i = n_i R T_i & P_f V_f = n_f R T_f \end{array}$$

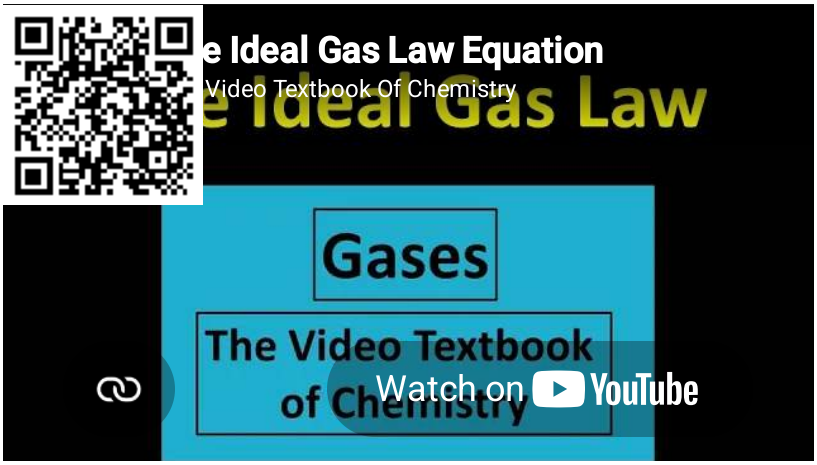
Both equations can be rearranged to give:

$$R = \frac{P_i V_i}{n_i T_i} \qquad R = \frac{P_f V_f}{n_f T_f}$$

The two equations are equal to each other since each is equal to the same constant R. Therefore, we have:

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f} \tag{11.4.8}$$

The equation is called the **general gas equation**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions. In such cases, the equation can be simplified by eliminating these constant gas properties.



Example 11.4.2

Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was −10°C (14°F). How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example 11.4.1?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A. Use the results from Example 11.4.1 for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 30°C to −10°C. Begin by constructing a table showing the initial and final conditions.

B. Simplify the general gas equation by eliminating the quantities that are held constant between the initial and final conditions, in this case P and n.

C. Solve for the unknown parameter.

Solution:

A To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

Solution to Example 10.4.2

Initial (August)	Final (January)
$T_i = 30\,°C = 303\,K$	$T_f = -10\,°C = 263\,K$
$P_i = 0.980\,atm$	$P_f = 0.980\,atm$
$n_i = 1.23 \times 10^3\,mol$	$n_f = 1.23 \times 10^3\,mol$
$V_i = 31150\,L$	V_f =?

B Both n and P are the same in both cases ($n_i = n_f, P_i = P_f$). Therefore, Equation 11.4.8 can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$\begin{aligned} V_f &= V_i \times \frac{T_f}{T_i} \\ &= 31150 \text{ L} \times \frac{263 \text{ K}}{303 \text{ K}} \\ &= 2.70 \times 10^4 \ L \end{aligned}$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume must be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

? Exercise 11.4.2

At a laboratory party, a helium-filled balloon with a volume of 2.00 L at 22°C is dropped into a large container of liquid nitrogen (T = −196°C). What is the final volume of the gas in the balloon?

Answer

0.52 L

Example 11.4.1 illustrates the relationship originally observed by Charles. We could work through similar examples illustrating the inverse relationship between pressure and volume noted by Boyle (*PV* = constant) and the relationship between volume and amount observed by Avogadro (*V*/*n* = constant). We will not do so, however, because it is more important to note that the historically important gas laws are only special cases of the ideal gas law in which two quantities are varied while the other two remain fixed. The method used in Example 11.4.1 can be applied in *any* such case, as we demonstrate in Example 11.4.2 (which also shows why heating a closed container of a gas, such as a butane lighter cartridge or an aerosol can, may cause an explosion).

✔ Example 11.4.3

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the “empty” aerosol can in Exercise 11.4.1 (0.025 mol in 0.406 L, initially at 25°C and 1.5 atm internal pressure) into a fire at 750°C. What would be the pressure inside the can (if it did not explode)?

Given: initial volume, amount, temperature, and pressure; final temperature

Asked for: final pressure

Strategy:

Follow the strategy outlined in Example 11.4.2.

Solution:

Prepare a table to determine which parameters change and which are held constant:

Solution to Example 10.4.3

Initial	Final
$V_i = 0.406$ L	$V_f = 0.406$ L
$n_i = 0.025$ mol	$n_f = 0.025$ mol
$T_i = 25$ °C $= 298$ K	$T_i = 750$ °C $= 1023$ K
$P_i = 1.5$ atm	$P_f =?$

Both V and n are the same in both cases ($V_i = V_f, n_i = n_f$). Therefore, Equation can be simplified to:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

By solving the equation for P_f, we get:

$$\begin{aligned} P_f &= P_i \times \frac{T_f}{T_i} \\ &= 1.5 \text{ atm} \times \frac{1023 \text{ K}}{298 \text{ K}} \\ &= 5.1 \; atm \end{aligned}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

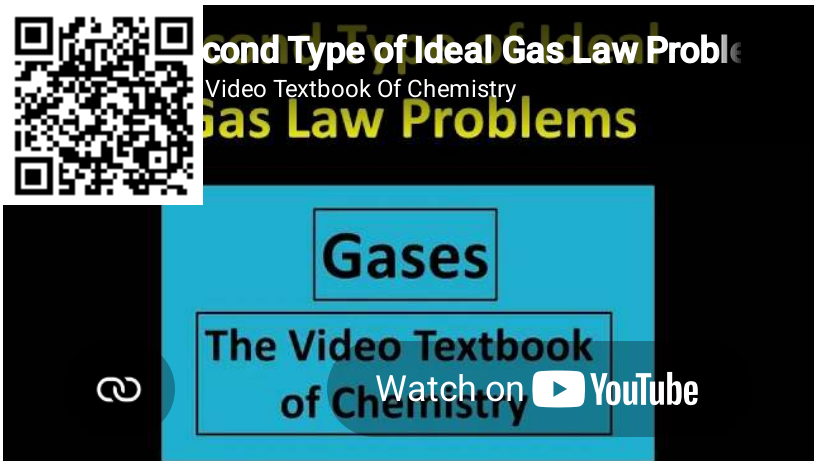
? Exercise 11.4.3

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

Answer

23.4 atm

In Examples 11.4.1 and 11.4.2, two of the four parameters (*P*, *V*, *T*, and *n*) were fixed while one was allowed to vary, and we were interested in the effect on the value of the fourth. In fact, we often encounter cases where two of the variables *P*, *V*, and *T* are allowed to vary for a given sample of gas (hence *n* is constant), and we are interested in the change in the value of the third under the new conditions.



Example 11.4.4

We saw in Example 11.4.1 that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained 1.23×10^3 mol of H_2 gas initially at 30°C and 745 mmHg. Suppose that Gay-Lussac had also used this balloon for his record-breaking ascent to 23,000 ft and that the pressure and temperature at that altitude were 312 mmHg and −30°C, respectively. To what volume would the balloon have had to expand to hold the same amount of hydrogen gas at the higher altitude?

Given: initial pressure, temperature, amount, and volume; final pressure and temperature

Asked for: final volume

Strategy:

Follow the strategy outlined in Example 11.4.3.

Solution:

Begin by setting up a table of the two sets of conditions:

Solution to Example 10.4.4

Initial	Final
$P_i = 745\ \text{mmHg} = 0.980\ \text{atm}$	$P_f = 312\ \text{mmHg} = 0.411\ \text{atm}$
$T_i = 30\ ^\circ\text{C} = 303\ \text{K}$	$T_f = 750 - 30\ ^\circ\text{C} = 243\ \text{K}$
$n_i = 1.2 \times 10^3\ \text{mol}$	$n_i = 1.2 \times 10^3\ \text{mol}$
$V_i = 31150\ \text{L}$	$V_f = ?$

By eliminating the constant property (n) of the gas, Equation 11.4.8 is simplified to:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

By solving the equation for V_f, we get:

$$\begin{aligned} V_f &= V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} \\ &= 3.115 \times 10^4\ \text{L} \times \frac{0.980\ \text{atm}}{0.411\ \text{atm}}\frac{243\ \text{K}}{303\ \text{K}} \\ &= 5.96 \times 10^4\ L \end{aligned}$$

Does this answer make sense? Two opposing factors are at work in this problem: decreasing the pressure tends to *increase* the volume of the gas, while decreasing the temperature tends to *decrease* the volume of the gas. Which do we expect to predominate? The pressure drops by more than a factor of two, while the absolute temperature drops by only about 20%. Because the volume of a gas sample is directly proportional to both *T* and 1/*P*, the variable that changes the most will have the greatest effect on *V*. In this case, the effect of decreasing pressure predominates, and we expect the volume of the gas to increase, as we found in our calculation.

We could also have solved this problem by solving the ideal gas law for *V* and then substituting the relevant parameters for an altitude of 23,000 ft:

Except for a difference caused by rounding to the last significant figure, this is the same result we obtained previously. *There is often more than one "right" way to solve chemical problems.*

Exercise 11.4.4

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

Answer

4.07×10^3

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

$$\frac{n}{V} = \frac{P}{RT} \tag{11.4.9}$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (m, in grams) divided by its molar mass (M, in grams per mole):

$$n = \frac{m}{M} \tag{11.4.10}$$

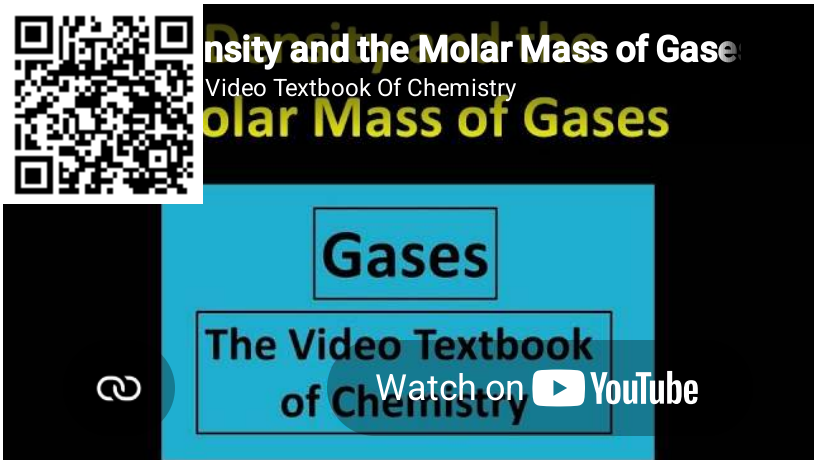
Substituting this expression for n into Equation 11.4.9 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{11.4.11}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$\rho = \frac{m}{V} = \frac{MP}{RT} \tag{11.4.12}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).



Example 11.4.5

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

Given: compound, temperature, and pressure

Asked for: density

Strategy:

A. Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.

B. Substitute these values into Equation 11.4.12 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$M = (4)(12.011) + (10)(1.0079) = 58.123 \text{g/mol}$$

Using 0.08206 (L•atm)/(K•mol) for R means that we need to convert the temperature from degrees Celsius to kelvins (T = 25 + 273 = 298 K) and the pressure from millimeters of mercury to atmospheres:

$$P = 750 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.987 \text{ atm}$$

B Substituting these values into Equation 11.4.12 gives

$$\rho = \frac{58.123 \text{ g/mol} \times 0.987 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}} = 2.35 \text{ g/L}$$

? Exercise 11.4.5: Density of Radon

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

Answer

radon, 9.23 g/L; N_2, 1.17 g/L

A common use of Equation 11.4.12 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and reweighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example 11.4.6.

✓ Example 11.4.6

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of 157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

Given: pressure, temperature, mass, and volume

Asked for: molar mass and chemical formula

Strategy:

A. Solve Equation 11.4.12 for the molar mass of the gas and then calculate the density of the gas from the information given.

B. Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.

C. Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 11.4.12 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P}$$

Density is the mass of the gas divided by its volume:

$$\rho = \frac{m}{V} = \frac{0.289\text{g}}{0.157\text{L}} = 1.84\text{g/L}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K$$

$$P = 727\,mmHg \times \frac{1\text{atm}}{760\text{mmHg}} = 0.957\text{atm}$$

The molar mass of the unknown gas is thus

$$M = \frac{1.84\text{ g/L} \times 0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol}$$

C The atomic masses of N and O are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$M(\text{NO}) = 14 + 16 = 30\text{ g/mol}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\text{ g/mol}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\text{ g/mol}$$

The most likely choice is NO_2 which is in agreement with the data. The red-brown color of smog also results from the presence of NO_2 gas.

? Exercise 11.4.6

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C; density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

Answer

44 g/mol; CO_2

Summary

The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

Ideal gas equation: $PV = nRT$,

where $R = 0.08206\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} = 8.3145\frac{\text{J}}{\text{K}\cdot\text{mol}}$

General gas equation: $\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$

Density of a gas: $\rho = \frac{MP}{RT}$

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, *PV* = *nRT*. The proportionality constant, *R*, is called the **gas constant** and has the value 0.08206 (L•atm)/(K•mol), 8.3145 J/(K•mol), or 1.9872 cal/(K•mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of

gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (*P*, *V*, *T*, or *n*) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of *P*, *V*, *T*, and *n*) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

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11.5: Applications of the Ideal Gas Law- Molar Volume, Density and Molar Mass of a Gas

Learning Objectives

- Apply gas laws to solve stoichiometry problems.
- Apply principles of stoichiometry to calculate properties of gases.

The quantitative relationship of reactants and products is called **stoichiometry**. Stoichiometric problems require you to calculate the amounts of reactants required for certain amounts of products, or amounts of products produced from certain amounts of reactants. If, in a chemical reaction, one or more reactants or products are gases, gas laws must be considered for the calculation. Usually, the applications of the ideal gas law give results within 5% precision. Below, we review several important concepts that are helpful for solving Stoichiometry Problems Involving Gases.

The Mole Concept and Molar Volume

The **mole** concept is the key to both stoichiometry and gas laws. A mole is a definite amount of substance. Mole is a unit based on the number of identities (i.e. atoms, molecules, ions, or particles). A mole of anything has the same number of identities as the number of atoms in exactly 12 grams of carbon-12, the most abundant isotope of carbon.

Molar volume is defined as the volume occupied by one mole of a gas. Using the ideal gas law and assuming standard pressure and temperature (STP), the volume of one mole of gas can be calculated:

$$PV = nRT \tag{11.5.1}$$

$$V = \frac{nRT}{P} \tag{11.5.2}$$

$$V = \frac{1.00\text{mol} \cdot 0.08206\frac{\text{Latm}}{\text{molK}} \cdot 273\text{K}}{1.00\text{atm}} \tag{11.5.3}$$

$$V = 22.4\text{L} \tag{11.5.4}$$

In other words, 1 mole of a gas will occupy 22.4 L at STP, assuming ideal gas behavior.

At STP, the volume of a gas is only dependent on number of moles of that gas and is independent of molar mass. With this information we can calculate the density (ρ) of a gas using only its molar mass. First, starting with the definition of density

$$\rho = \frac{m}{V} \tag{11.5.5}$$

we rearrange for volume:

$$V = \frac{m}{\rho} \tag{11.5.6}$$

We then substitute V into the ideal gas equation and rearrange for density:

$$PV = nRT \tag{11.5.7}$$

$$P\frac{m}{\rho} = nRT \tag{11.5.8}$$

$$\rho = \frac{mP}{nRT} \tag{11.5.9}$$

Finally, we remember that molar mass is equal to mass divided by number of moles:

$$MM = \frac{m}{n} \tag{11.5.10}$$

and substitute this into our expression for density to give:

$$\rho = \frac{MM \cdot P}{RT} \tag{11.5.11}$$

This equation can further be simplified if we assume STP:

$$\rho = \frac{MM \cdot 1\text{atm}}{(0.08206\frac{\text{Latm}}{\text{molK}})273\text{K}} \tag{11.5.12}$$

$$\rho = \frac{MM}{22.4\frac{\text{L}}{\text{mol}}} \tag{11.5.13}$$

Using this information, we can calculate the density of a gas using the gas's molar mass.

Example 1

Calculate the density of N_2 gas at STP.

What we know: Pressure (1 atm),temperature (273 K), the identity of the gas (N_2).

Asked for: Density of N_2

Strategy:

A. Calculate the molar mass of N_2
B. Solve for the density of using the equation relating density and molar mass at STP

Solution:

A The molar mass of N_2:

$$MM_{N2} = 2 \cdot 14.0\text{g/mol} = 28.0\text{g/mol} \tag{11.5.14}$$

B Calculate the density of N_2

$$\rho = \frac{MM}{22.4\frac{\text{L}}{\text{mol}}} \tag{11.5.15}$$

$$\rho = \frac{28.0\text{g/mol}}{22.4\frac{\text{L}}{\text{mol}}} \tag{11.5.16}$$

$$\rho = 1.25\text{g/L} \tag{11.5.17}$$

Example 2

Calculate the density of Ne gas at 143 ºC and 4.3 atm.

What we know: Pressure (4.3 atm), temperature (143 ºC), the identity of the gas (Ne), the molar mass of Ne from the periodic table (20.2 g/mol).

Asked for: Density of Ne

Strategy:

A. The temperature is given in degrees Celsius. This must be converted to Kelvin
B. Solve for the density

Solution:

A Calculate temperature in Kelvin:

$$T = 143\text{C} + 273 = 416\text{K} \tag{11.5.18}$$

B Calculate the density of Ne:

$$\rho = \frac{MM \cdot P}{RT} \tag{11.5.19}$$

$$\rho = \frac{20.2\text{g/mol} \cdot 4.3\text{atm}}{(0.08206\frac{\text{Latm}}{\text{molK}})416\text{K}} \tag{11.5.20}$$

$$\rho = 2.54\text{g/L} \tag{11.5.21}$$

Molar Mass of a Gas

The equations for calculating the density of a gas can rearranged to calculate the molar mass of a gas:

$$MM = \frac{\rho RT}{P} \tag{11.5.22}$$

this can be further simplified if we work at STP:

$$MM = \rho \cdot 22.4L/mol \tag{11.5.23}$$

We can use these equations to identify an unknown gas, as shown below:

Example 3

A unknown gas has density of 1.78 g/L at STP. What is the identify of this gas?

What we know: Pressure (1.00 atm), temperature (273 K), density of the gas (1.783 g/L)

Asked for: Identity of the unknown gas

Strategy:

A. First calculate the molar mass of the unknown gas
B. Determine the identity of the gas by comparing the calculated molar mass to molar masses of known gases.

Solution:

A Since we are at STP, we can use the following equation to calculate molar mass:

$$MM = \rho \cdot 22.4L/mol \tag{11.5.24}$$

$$MM = 1.783\text{g/L} \cdot 22.4\text{L/mol} \tag{11.5.25}$$

$$MM = 39.9\text{g/mol} \tag{11.5.26}$$

B The calculated molar mass is 33.9 g/mol. Examination of the periodic table reveals that Argon has a mass of 39.948 g/mol. Therefore, the unknown gas is most likely argon.

Stoichiometry and Gas Laws

Stoichiometry is the theme of the previous block of modules, and the ideal gas law is the theme of this block of modules. These subjects are related. Be prepared to solve problems requiring concepts or principles of stoichiometry and gases. For example, we can calculate the number of moles from a certain volume, temperature and pressure of a HCl gas. When *n* moles are dissolved in *V* L solution, its concentration is *n/V* M.

Three examples are given to illustrate some calculations of stoichiometry involving gas laws and more are given in question form for you to practice.

Example 1

If 500 mL of HCl gas at 300 K and 100 kPa dissolve in 100 mL of pure water, what is the concentration? Data required: R value 8.314 kPa L / (K mol).

Solution

$$n_{HCl} = \frac{0.50\ \text{L} \times 100\ \text{kPa}}{8.314\ \frac{\text{kPa L}}{\text{K mol}} \times 300\ \text{K}} \tag{11.5.27}$$

$$= 0.02\ \text{mol} \tag{11.5.28}$$

Concentration of HCl, $[HCl]$

$$[HCl] = \frac{0.02\ \text{mol}}{0.1\ \text{L}} = 0.2\ \text{mol/L}$$

Discussion

Note that R = 0.08205 L atm /(K mol) will not be suitable in this case. If you have difficulty, review Solutions.

Example 2

If 500 mL of HCl gas at 300 K and 100 kPa dissolved in pure water requires 12.50 mL of the $NaOH$ solution to neutralize in a titration experiment, what is the concentration of the $NaOH$ solution?

Solution

Solution in Example 1 showed n_{HCl} = 0.02 mol. From the titration experiment, we can conclude that there were 0.02 moles of $NaOH$ in 12.50 mL. Thus,

$$[NaOH] = \frac{0.02\ \text{mol}}{0.0125\ \text{L}} = 1.60\ \text{mol/L}$$

Discussion

Think in terms of reaction,

$$HCl + NaOH \rightarrow NaCl + H_2O \Leftarrow \text{Reaction} \tag{11.5.29}$$

$$0.02\ \text{mol}\ \ 0.02\ \text{mol} \qquad \Leftarrow \text{Quantities reacted} \tag{11.5.30}$$

Note that 0.02 mol of $NaOH$ is in 0.0125 mL solution.

Example 3

A 5.0-L air sample containing H_2S at STP is treated with a catalyst to promote the reaction

$$H_2S + O_2 \rightarrow H_2O + S_{(solid)}.$$

If 3.2 g of solid S was collected, calculate the volume percentage of H_2S in the original sample.

Solution

$$3.2\ \text{g S} \times \frac{1\ \text{mol}\ H_2S}{32\ \text{g S}} = 0.10\ \text{mol}\ H_2S$$

$$V_{H_2S} = 0.10\ \text{mol} \times 22.4\ \text{L/mol} \tag{11.5.31}$$

$$= 2.24\ \text{L} \tag{11.5.32}$$

$$\text{Volume}\ \% = \frac{2.25\ \text{L}}{5.0\ \text{L}} \tag{11.5.33}$$

$$= 0.45 \tag{11.5.34}$$

$$= 45\% \tag{11.5.35}$$

Discussion

Data required: Atomic mass: $H = 1$; $O = 16$; $S = 32$. R = 0.08205 L atm /(K mol) is now suitable R values or molar volume at STP (22.4 L/mol)

The volume percentage is also the mole percentage, but not the weight percentage.

Example 4

Hydrogen sulfide reacts with sulfur dioxide to give H_2O and S,

$$H_2S + SO_2 \rightarrow H_2O + S_{(solid)}, \text{ unbalanced.}$$

If 6.0 L of H_2S gas at 750 torr produced 3.2 g of sulfur, calculate the temperature in C.

Solution

Balanced reaction:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S_{(solid)}$$
$$2 \text{ mol} \qquad 3 \times 32 = 96 \text{ g}$$

$$3.2 \text{ g S} \times \frac{2 \text{ mol } H_2S}{96 \text{ g S}} = 0.067 \text{ mol } H_2S$$

$$P = \frac{750}{760} = 0.987 \text{ atm}$$

$$T = \frac{PV}{nR} = \frac{0.987 \text{ atm} \times 6 \text{ L}}{0.067 \text{ mol} \times 0.08205 \frac{\text{atm L}}{\text{mol K}}} \tag{11.5.36}$$
$$= 1085 \text{ K} \tag{11.5.37}$$
$$= 812^\circ\text{C} \tag{11.5.38}$$

Discussion

Atomic mass: H = 1.0; O = 16.0; S = 32.0. *R* = 0.08205 L atm /(K mol) is OK but watch units used for pressure.

Example 5

When 50.0 mL of $AgNO_3$ solution is treated with an excess amount of HI gas to give 2.35 g of AgI, what is the concentration of the $AgNO_3$ solution?

Solution

$$2.35 \text{ g AgI} \times \frac{1 \text{ mol } Ag^+}{234.8 \text{ g AgI}} \times \frac{1 \text{ mol } AgNO_3}{1 \text{ mol } Ag^+} = 0.010 \text{ mol } AgNO_3$$

$$[AgNO_3] = \frac{0.01 \text{ mol } AgNO_3}{0.050 \text{ L}} \tag{11.5.39}$$
$$= 0.20 \text{ M } AgNO_3 \tag{11.5.40}$$

Discussion

A gas is involved, but there is no need to consider the gas law. At. mass: Ag = 107.9; N = 14.0; O = 16.0; I = 126.9

Example 6

What volume (L) will 0.20 mol HI occupy at 300 K and 100.0 kPa? $R = 8.314 \frac{\text{kPa L}}{\text{K mol}} = 0.08205 \frac{\text{atm L}}{\text{mol K}}$

Solution

$$V = \frac{nRT}{P} \tag{11.5.41}$$
$$= \frac{0.20 \text{ mol} \times 8.314 \frac{\text{kPa L}}{\text{mol K}} \times 300 \text{ K}}{100 \text{ kPa}} \tag{11.5.42}$$
$$= 5 \text{ L} \tag{11.5.43}$$

Example 7

A 3.66-g sample containing Zn (at.wt. 65.4) and Mg (24.3) reacted with a dilute acid to produce 2.470 L H_2 gas at 101.0 kPa and 300 K. Calculate the percentage of Zn in the sample.

Solution

The number of moles of gas produced is the number of moles of metals in the sample. Once you know the number of moles, set up an equation to give the number of moles of metal in the sample.

$$n = \frac{101\ \text{kPa} \times 2.470\ \text{L}}{8.3145\ \frac{\text{kPa L}}{\text{mol K}} \times 300\ \text{K}} \tag{11.5.44}$$

$$= 0.100\ \text{mol} \tag{11.5.45}$$

Let *x* be the mass of Zn, then the mass of Mg is 3.66 - *x* g. Thus, we have

$$\frac{x}{65.4} + \frac{3.66 - x}{24.3} = 0.100\ \text{mole}$$

Solving for *x* gives *x* = 1.96 g Zn,

and the $\text{weight percent} = 100 \times \frac{1.96}{3.66} = 53.6\%$

Discussion

Find the mole percent of Zn in the sample.

$$\#\ \text{mol of Zn} = \frac{1.96}{65.4} = 0.03\ \text{mol}$$

$$\#\ \text{mol of Mg} = \frac{1.70}{24.3} = 0.07\ \text{mol}$$

$$\text{mole percent} = 100 \times \frac{0.03}{0.03 + 0.07} = 30\%$$

Example 8

When a 2.00 g mixture of Na and Ca reacted with water, 1.164 L hydrogen was produced at 300.0 K and 100.0 kPa. What is the percentage of Na in the sample?

Solution

$$2\,\text{Na} + 2\,\text{H}_2\text{O} \rightarrow 2\,\text{Na(OH)} + \text{H}_{2(g)}$$

$$\text{Ca} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)} + \text{H}_{2(g)}$$

Let x be the mass of Na, then (2.00-x) is the mass of Ca.

We have the following relationship

$$\frac{\text{x g}}{23.0\ \text{g/mol}} \times \frac{1\ \text{mol H}_2}{2\ \text{mol Na}} + \frac{(2.0 - \text{x})\ \text{g Ca}}{40.1\ \text{g Ca/mol}} \times \frac{1\ \text{mol H}_2}{1\ \text{mol Ca}} = \frac{1.164\ \text{L H}_2 \times 100.0\ \text{kPa}}{8.3145\ \text{kPa L mol}^{-1}\ \text{K}^{-1}\ 300.0\ \text{K}}$$

Simplify to give

$$\frac{\text{x}}{46.0} + \frac{2}{40.1} - \frac{\text{x}}{40.1} = 0.0467\ \text{all in mol}$$

Multiply all terms by (40.1 * 46.0)

$$40.1\,\text{x} + 2 \times 46.0 - 46.0\,\text{x} = 86.1$$

Simplify

$$-5.9\,\text{x} = 86.1 - 92.0 = -5.91$$

Thus,

$$\text{Mass of Na} = \text{x} = 1.0\ \text{g}$$

$$\text{Mass of Ca} = 2.0 - \text{x} = 1.0\ \text{g}$$

$$\text{Mass Percentage of Na} = 100 \times \frac{1}{2.0} = 50\%$$

Discussion

$$\text{Mole of Na} = \frac{1}{23} = 0.0435\ \text{mol}$$

$$\text{Mole percentage} = \frac{\frac{1}{23}}{\frac{1}{23} + \frac{1}{40.1}} = 0.635 = 63.5\%$$

Compare this example with gravimetric analyses using the reaction

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

where $Cl^-_{(aq)}$ comes from the disolution of two salts such as $NaCl$ and $MgCl_2$.

Also compare with analyses making use of the reaction

$$Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow BaSO_{4(s)}$$

where the anion $SO^{2-}_{4(aq)}$ comes from the dissolution of two sulfate salts.

This example is very similar to Example 7.

Contributors and Attributions

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11.6: Mixtures of Gases and Partial Pressures

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. The Learning Objective of this module is to determine the contribution of each component gas to the total pressure of a mixture of gases.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{10.6.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize,**the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases**. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton's law of partial pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{10.6.2}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

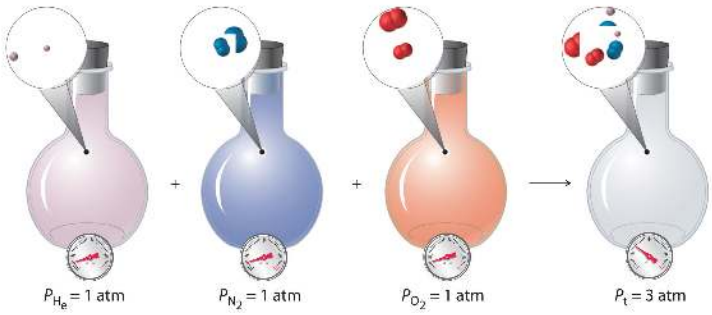


Figure Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{10.6.3}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{10.6.2a}$$

$$P_{tot} = \sum_{i=1}^{n} n_i\left(\frac{RT}{V}\right) \tag{10.6.2b}$$

Equation 10.6.4 restates Equation 10.6.3 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 10.6.4 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 the example below:

Example

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. **Solution:**

$$n_{\text{He}} = \frac{326.4\ \text{g}}{4.003\ \text{g/mol}} = 81.54\ \text{mol} \tag{11.6.1}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2\ \text{g}}{32.00\ \text{g/mol}} = 1.60\ \text{mol} \tag{11.6.2}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} = \frac{81.54\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 196.2\ \text{atm} \tag{11.6.3}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} = \frac{1.60\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 3.85\ \text{atm} \tag{11.6.4}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85)\ \text{atm} = 200.1\ \text{atm} \tag{11.6.5}$$

Exercise 10.6.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer: $P_{CH_4} = 137\ atm$; $P_{C_2H_6} = 13.4\ atm$; $P_{tot} = 151\ atm$

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}):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{10.6.5}$$

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: $P_A = n_A RT/V$ and $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{10.6.6}$$

Rearranging this equation gives

$$P_A = x_A P_{tot} \tag{10.6.7}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 10.6.7, 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

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 10.6.7.
Solution:
The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}} \tag{11.6.6}$$

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:

$$x_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063 \tag{11.6.7}$$

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 10.6.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.
Answer

$$P_{CO_2} = 86 \text{ atm}, P_{N_2} = 2.7 \text{ atm}$$

Summary

- 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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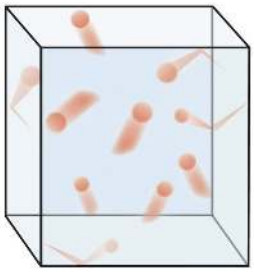
11.7: A Particulate Model for Gases- Kinetic Molecular Theory

The Learning Objective of this Module is 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. 

   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.

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.

- $$P_1V_1 = P_2V_2 \tag{11.7.1}$$
  - $$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{11.7.2}$$
    - $$P_{total} = P_a + P_b + P_c + ... \tag{11.7.3}$$

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11.8: Temperature and Molecular Velocities

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? . This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure 10.7.1. 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 10.7.1 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.

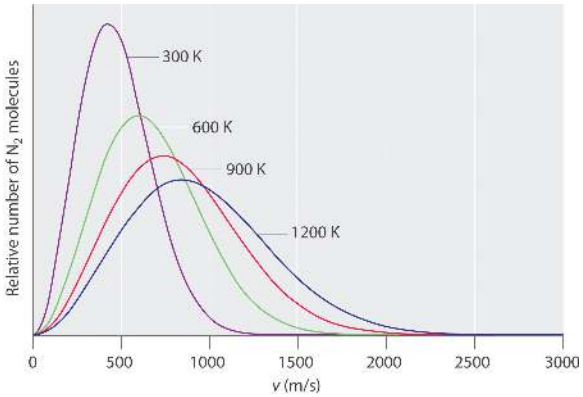


Figure 10.7.2 The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

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11.9: Mean Free Path, Diffusion, and Effusion of Gases

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*:*

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{M_B}{M_A}}. \tag{11.9.1}$$



Ethylene oxide

Heavy molecules effuse through a porous material more slowly than light molecules, as illustrated schematically in Figure 10.8.1 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.

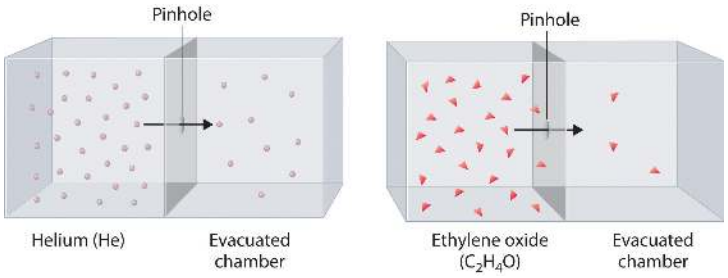


Figure 10.8.1 The Relative Rates of Effusion of Two Gases with Different Masses. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.

Note

At a given temperature, heavier molecules move more slowly than lighter molecules.

Example 10.8.1

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. **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 $^{235}UF_6$
   A. **Solution:**
      1. The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is 234.04 + (6)(18.998) = 349.03 g/mol 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.

$$\frac{\text{rate } ^{235}UF_6}{\text{rate } ^{238}UF_6} = \sqrt{\frac{352.04 \text{ g/mol}}{349.03 \text{ g/mol}}} = 1.0043 \tag{11.9.2}$$



Figure *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.*

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:

$$KE = \frac{1}{2}\frac{M_A}{N_A}v_{rms,A}^2 = \frac{1}{2}\frac{M_B}{N_A}v_{rms,B}^2 \tag{10.8.1}$$

Multiplying both sides by 2 and rearranging give

11.9: Mean Free Path, Diffusion, and Effusion of Gases is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

11.10: Gases in Chemical Reactions- Stoichiometry Revisited

Earlier in the course we performed stoichiometric calculations with chemical reactions using quantities of moles and mass (typically in grams). These same principles can be applied to chemical reactions involving gases except that we first have to convert volumes of gases into moles.

Example

Hydrogen gas reacts with oxygen gas to produce water vapor via the following balanced chemical equation:
$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$
If the temperature is 320 K and pressure is 1.34 atm, what volume of oxygen is required to produce 65.0 g of water?
Strategy: Since we are given the temperature and pressure, to find the volume of oxygen using the ideal gas law we need to first calculate the moles of oxygen. To find the moles of oxygen required, we can first calculate the moles of water in 65.0g.

$$n_{water} = \frac{m_{water}}{mm_{water}} = \frac{65.0\text{ g}}{18.0\text{g/mol}} = 3.61\text{ mol of water} \tag{11.10.1}$$

From the balanced chemical equation, we can see that 1 equivalent of oxygen produces 2 equivalents of water. We can therefore write the following ratio:
1 mol O_2 : 2 mol H_2O
We can now solve for the amount of oxygen:

$$(3.61\text{ mol } H_2O) \times (\frac{1\text{ mol } O_2}{2\text{ mol } H_2O}) = 1.81\text{ mol } O_2 \tag{11.10.2}$$

Finally, now that we know how many moles of oxygen are required, we can calculate the volume of the oxygen using the ideal gas law and the temperature&pressure provided in question:

$$PV = nRT \tag{11.10.3}$$

$$V = \frac{nRT}{P} \tag{11.10.4}$$

$$V = \frac{1.81\text{mol } \cdot 0.08206\frac{\text{Latm}}{\text{molK}} \cdot 320\text{K}}{1.34\text{atm}} \tag{11.10.5}$$

$$V = 35.5\text{L} \tag{11.10.6}$$

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11.11: Real Gases- The Effects of Size and Intermolecular Forces

Learning Objectives

- To recognize the differences between the behavior of an ideal gas and a real gas
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (Figure 11.11.1a). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (Figure 11.11.1b).

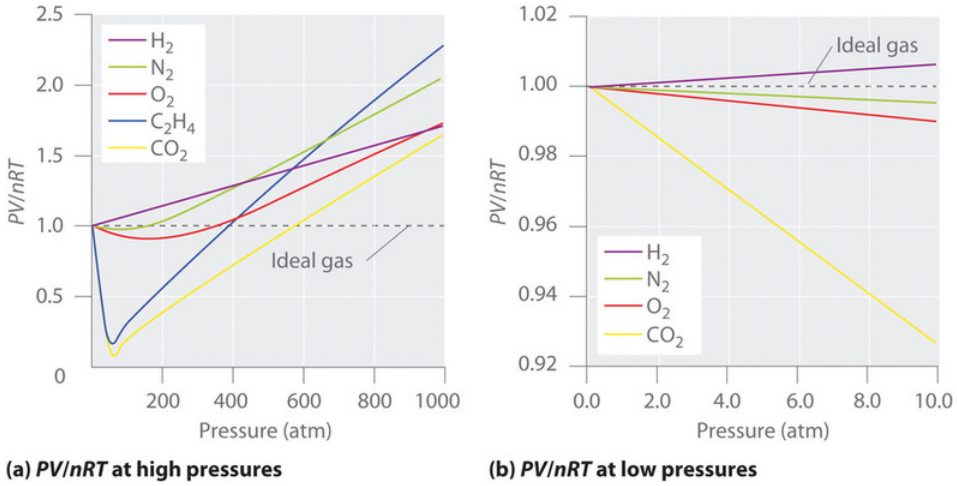


Figure 11.11.1: Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of *PV*/*nRT* versus *P* at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate 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 11.11.2 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.

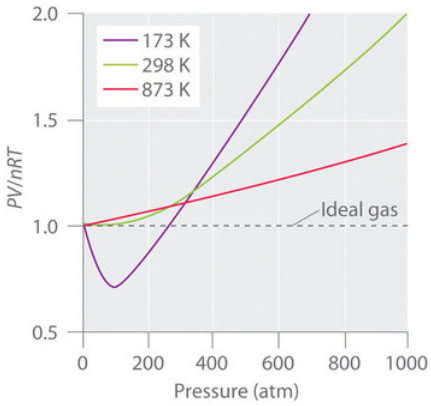


Figure 11.11.2: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

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 11.11.3). 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.

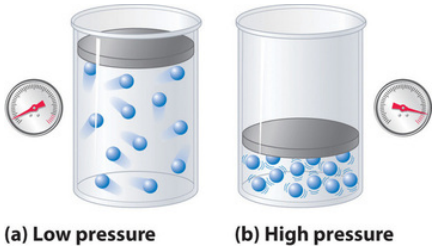


Figure 11.11.3: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure 11.11.4). Thus as shown in Figure 11.11.2, at low temperatures, the ratio of \(PV/nRT\) is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

> *Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.*

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas

behavior, the so-called *van der Waals* equation,

$$\underbrace{\left(P+\frac{an^2}{V^2}\right)}_{\text{Pressure Term}}\overbrace{(V-nb)}^{\text{Pressure Term}}=nRT \tag{11.11.1}$$

a and *b* are empirical constants that are different for each gas. The values of a and b are listed in Table 11.11.1 for several common gases.

Table 11.11.1:: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	*a* (L^2·atm)/mol^2)	*b* (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in Equation 11.11.1 corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure 11.11.4. The volume term corrects for the volume occupied by the gaseous molecules.

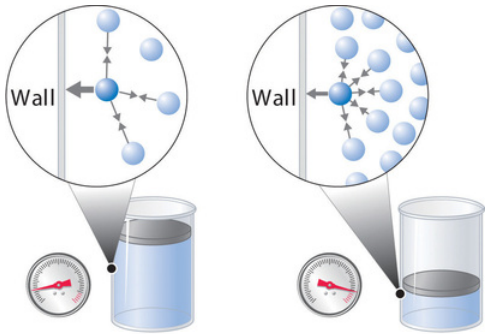


Figure 11.11.4: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close 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 11.11.1

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 11.11.1. Use the van der Waals equation (11.11.1) to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} \tag{11.11.2}$$

$$= \frac{500\ \text{g}}{70.906\ \text{g/mol}} \tag{11.11.3}$$

$$= 7.052\ mol$$

Using the ideal gas law and the temperature in kelvin (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} \tag{11.11.4}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} \tag{11.11.5}$$

$$= 43.1\ atm \tag{11.11.6}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table 11.11.1. Solving for P gives

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{11.11.7}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \frac{\text{L}}{\text{mol}}} - \frac{6.260 \frac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \tag{11.11.8}$$

$$= 28.2\ \text{atm} \tag{11.11.9}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise 11.11.1

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

Answer 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 in the van der Waals equation indicates the presence of relatively strong intermolecular attractive interactions.*

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids, from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing.” They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



Figure 11.11.5: A Liquid Natural Gas Transport Ship.

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure 11.11.5). 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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11.E: Exercises

11.5: Applications of the Ideal Gas Law: Molar Volume, Density and Molar Mass of a Gas

1. **If 100 mL of HCl gas at 300 K and 100 kPa dissolves in 20 mL of pure water, what is the concentration?**

   Hint: 0.4 mol/L

   Skill:
   Calculate *n* using ideal gas law.

2. **If 100 mL of HCl gas at 300 K and 100 kPa dissolved in pure water requires 12.50 mL of the NaOH solution to neutralize in a titration experiment, what is the concentration of the NaOH solution?**
   Hint: 0.32 mol/L

   Skill:
   Apply ideal gas law to solve stoichiometry problems.

3. **If 100 mL of HCl gas at 300 K and 200 kPa dissolved in pure water requires 12.50 mL of the NaOH solution to neutralize in a titration experiment, what is the concentration of the NaOH solution?**

   Hint: 0.64 mol/L

   Skill:
   Solve stoichiometric problem.

4. **Hydrogen sulfide reacts with sulfur dioxide to give $\mathrm{H_2O}$ and S,**

   $$\mathrm{H_2S + SO_2 \rightarrow H_2O + S_{(solid)}}, \text{ unbalanced}$$

   If 3.0 L of $\mathrm{H_2S}$ gas at 760 torr produced 4.8 g of sulfur, calculate the temperature in C.

   Hint: 93 degrees C

   Skill:
   Apply ideal gas law to solve stoichiometry problems.

5. **When 10.0 mL of $\mathrm{AgNO_3}$ solution is treated with excess amount of HI gas to give 0.235 g of AgI, what is the concentration of the $\mathrm{AgNO_3}$ solution?**

   Hint: 0.10 M

6. **When an $\mathrm{AgNO_3}$ solution is treated with 50.0 mL of HI gas to give 0.235 g of AgI, what is the concentration of the HI gas?**

   Hint: 0.020 mol/L

7. **When an $\mathrm{AgNO_3}$ solution is treated with 50.0 mL of HI gas at 300 K to give 0.235 g of AgI, what is the pressure of the HI gas?**

   Hint: 0.49 atm

   Discussion:
   Depending on the numerical values you use, you may get the pressure in other units.

8. **When an $\mathrm{AgNO_3}$ solution is treated with 50.0 mL of HI gas at 374 torr to give 0.235 g of AgI, what is the temperature of the HI gas?**

   Hint: 300 K

   Discussion:
   Note the relationship of this problem with the previous one.

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CHAPTER OVERVIEW

12: Liquids, Solids, and Intermolecular Forces

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- 12.1: Structure Determines Properties
- 12.2: Solids, Liquids, and Gases- A Molecular Comparison
- 12.3: Intermolecular Forces- The Forces that Hold Condensed Phases Together
- 12.4: Intermolecular Forces in Action- Surface Tension, Viscosity, and Capillary Action
- 12.5: Vaporization and Vapor Pressure
- 12.6: Sublimation and Fusion
- 12.7: Heating Curve for Water
- 12.8: Water - An Extraordinary Substance

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12.1: Structure Determines Properties

Here on Earth, we all live in a state of gravity. Not only us, but everything around us, including water, is being pulled towards the center of the planet by gravity. True, it is nice that our dogs don't float off into space, but when a child drops their ice cream (which is full of water, by the way) they don't have to know about gravity to be upset



***Floating Water in Zero Gravity**: Once again, astronauts on the International Space Station dissolved an effervescent tablet in a floating ball of water, and captured images using a camera capable of recording four times the resolution of normal high-definition cameras. The higher resolution images and higher frame rate videos can reveal more information when used on science investigations, giving researchers a valuable new tool aboard the space station. This footage is one of the first of its kind. The cameras are being evaluated for capturing science data and vehicle operations by engineers at NASA's Marshall Space Flight Center in Huntsville, Alabama.*

If you go far enough out in space, for instance, onto the International Space Station, gravity becomes negligible, and the laws of physics act differently than here on Earth. Just how might water act in a place of zero gravity? This video above from NASA gives you a good idea of how different water behaves when the effects if gravity are counteracted.

Actually, on the International Space Station, there is plenty of gravity—according to NASA scientists, the pull of Earth's gravity on the space station and its occupants is substantial: about 90 percent of the force at the Earth's surface. But since the space station is continuously falling around our planet, the astronauts and objects on board are in a kind of free-fall, too, and feel nearly weightless. Water on the space station behaves as if in a zero-gravity environment.

This unique picture shows not only a water drop but also an air bubble inside of the water drop. Notice they both behave the same....according to the laws of physics in space. They both form spheres. This makes sense, as without gravity to tug downward, the forces governing the objects are all the same. So, the water drop (and air bubble) form themselves so they occupy a shape having the least amount of surface area, which is a sphere. On Earth, gravity distorts the shape, but not in space.

Consider what would happen on Earth: The air bubble, lighter than water, would race upward to burst through the surface of the droplet. In space, the air bubble doesn't rise because it is no lighter than the water around it—there's no buoyancy. The droplet doesn't fall from the leaf because there's no force to pull it off. It's stuck there by molecular adhesion.

Sticky water. No buoyancy. These are some of the factors space-farers must take into account when they plan their space gardens. If water is sprayed onto the base of the plant will it trickle down to the roots? More likely it will stick to the stem or adhere to the material in which the plant grows. As humans spend more time and go farther out in space in the future, the physics of "space water" will need to be well understood.

Reference

- The Physics of Space Gardens, NASA.

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12.2: Solids, Liquids, and Gases- A Molecular Comparison

Learning Objectives

- To be familiar with the kinetic molecular description of liquids.

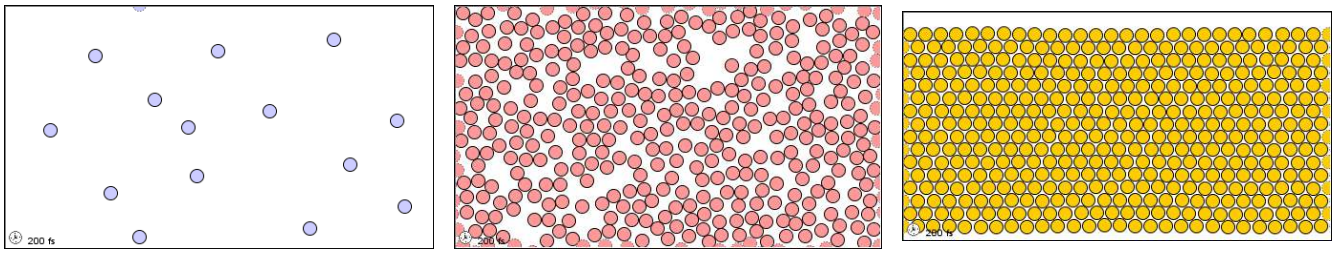
The *physical* properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same *chemical* properties, but their *physical* properties are considerably different. In general *covalent bonds* determine: molecular shape, bond energies, *chemical* properties, while *intermolecular forces* (non-covalent bonds) influence the *physical* properties of liquids and solids. The kinetic molecular theory of gases gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.



Figure 12.2.1: The three common states of matter. From the left, they are solid, liquid, and gas, represented by an ice sculpture, a drop of water, and the air around clouds, respectively. Images used with permission from Wikipedia.

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces are attractive forces that try to draw the particles together (Figure 12.2.2). A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.

Molecular level picture of gases, liquids and solids.



(a) in the gaseous state	*(b) as a liquid*	(c) *in solid form*

Figure 12.2.2: Molecular level picture of gases, liquids and solids.

Below is an overview of the general properties of the three different phases of matter.

Properties of Gases

- A collection of widely separated molecules
- The kinetic energy of the molecules is greater than any attractive forces between the molecules
- The lack of any significant attractive force between molecules allows a gas to expand to fill its container
- If attractive forces become large enough, then the gases exhibit non-ideal behavior

Properties of Liquids

- The intermolecular attractive forces are strong enough to hold molecules close together
- Liquids are more dense and less compressible than gasses
- Liquids have a definite volume, independent of the size and shape of their container
- The attractive forces are ***not*** strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

> *Thus, liquids can be poured and assume the shape of their containers.*

Properties of Solids

- The intermolecular forces between neighboring molecules are strong enough to keep them locked in position
- Solids (like liquids) are not very compressible due to the lack of space between molecules
- If the molecules in a solid adopt a highly ordered packing arrangement, the structures are said to be ***crystalline***

> *Due to the strong intermolecular forces between neighboring molecules, solids are rigid.*

- Cooling a gas may change the state to a liquid
- Cooling a liquid may change the state to a solid
- Increasing the pressure on a gas may change the state to a liquid
- Increasing the pressure on a liquid may change the state to a solid



Video 12.2.1: Video highlighting the properties for the three states of matter. Source found at www.youtube.com/watch?v=s-KvoVzukHo.

Physical Properties of Liquids

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described previously. This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers. A kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces. Solids and liquids have particles that are fairly close to one another, and are thus called "**condensed phases**" to distinguish them from gases

- **Density**: The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance. Densities of liquids are therefore

more commonly measured in units of grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.

- **Molecular Order:** Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids, the molecules in liquids are not arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.
- **Compressibility**: Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.
- **Thermal Expansion**: The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table S1 (with a shorten version in Table 12.2.1) that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

Table 12.2.1: The Density of Water at Various Temperatures

T (°C)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

- **Diffusion**: Molecules in liquids diffuse because they are in constant motion. A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.
- **Fluidity**: Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure 12.2.3).

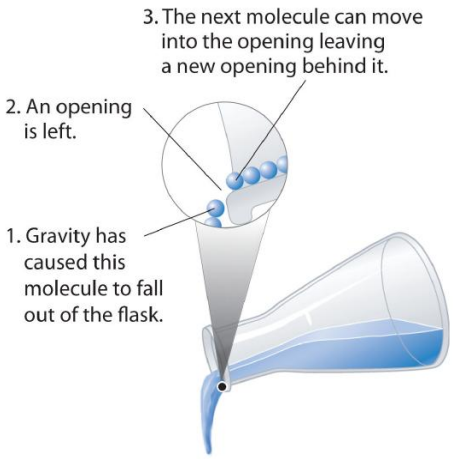


Figure 12.2.3: Why Liquids Flow. Molecules in a liquid are in constant motion. Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container. (CC BY-SA-NC; Anonymous vy request).

Contributors and Attributions

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12.3: Intermolecular Forces- The Forces that Hold Condensed Phases Together

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 $12.3.1a$.

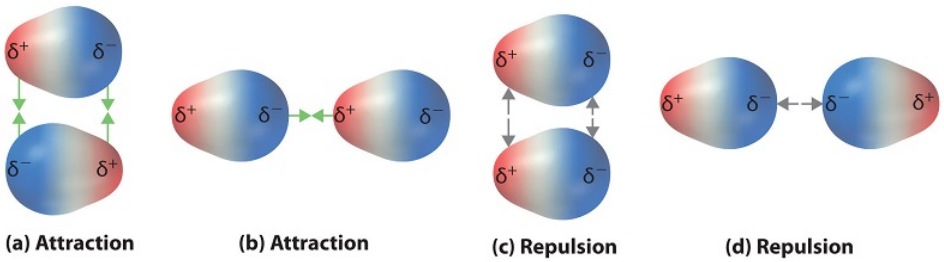


Figure 12.3.1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or 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 12.3.1*c*). Hence dipole–dipole interactions, such as those in Figure 12.3.1*b*, are *attractive intermolecular interactions*, whereas those in Figure 12.3.1*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 12.3.2. On average, however, the attractive interactions dominate.

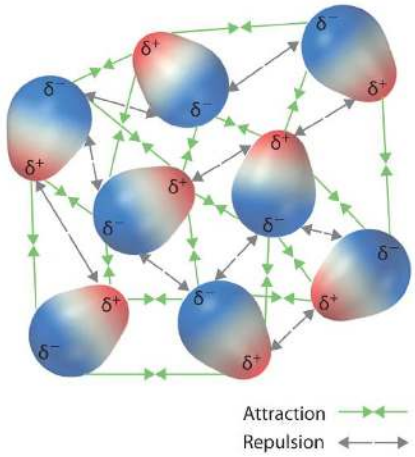


Figure 12.3.2: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

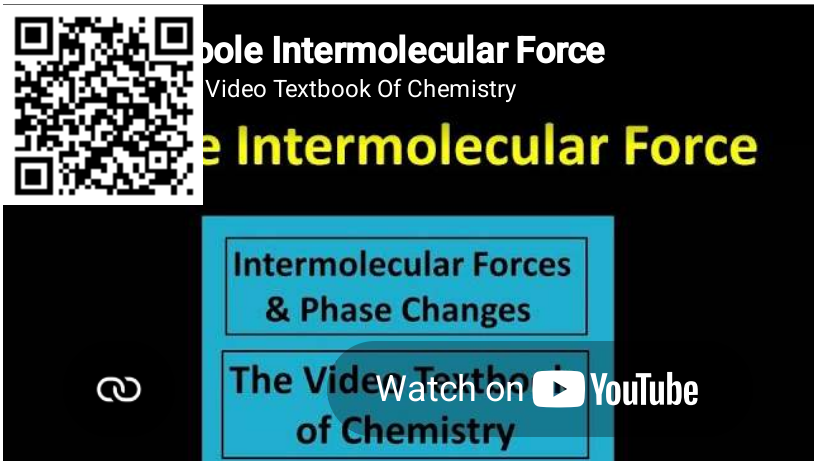
The green arrows pointing towards each other represent attraction. The gray arrows pointing away from each other represent repulsion

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 12.3.1.

Table 12.3.1: 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

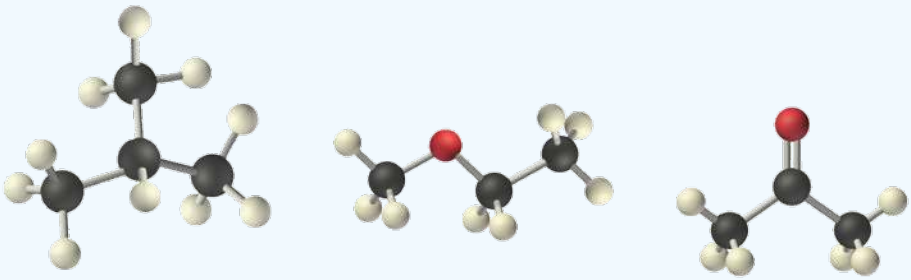
> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*



Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 12.3.1

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 12.3.1

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

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)

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 12.3.2).

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 12.3.2: 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 12.3.3, 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.

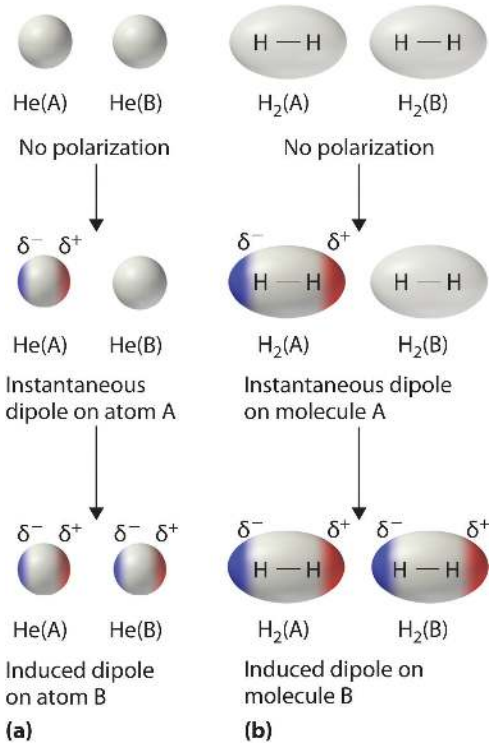


Figure 12.3.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

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 12.3.3, tends to become more pronounced as atomic and molecular masses increase (Table 12.3.2). 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 1*s* 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 12.3.4). 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 12.3.4 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).

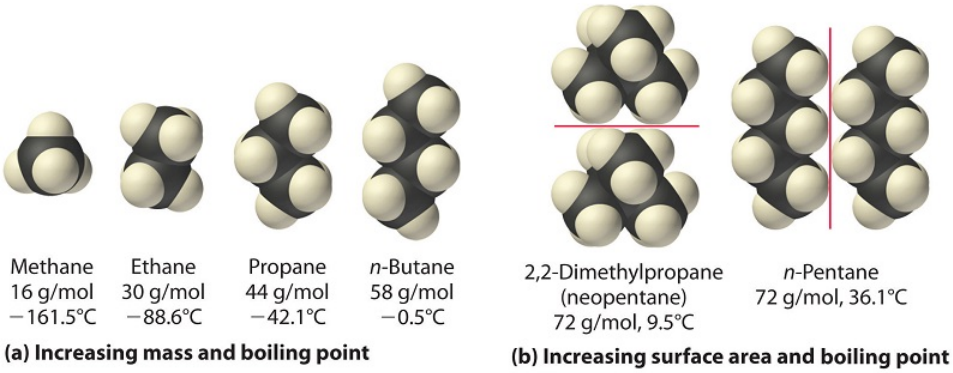
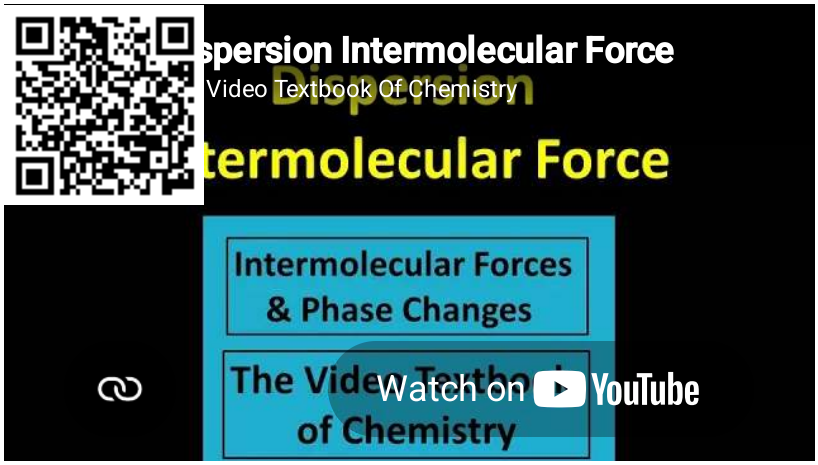


Figure 12.3.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger 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.



Video Discussing London/Dispersion Intermolecular Forces. Source: Dispersion Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 12.3.2

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 12.3.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

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 12.3.5. 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.

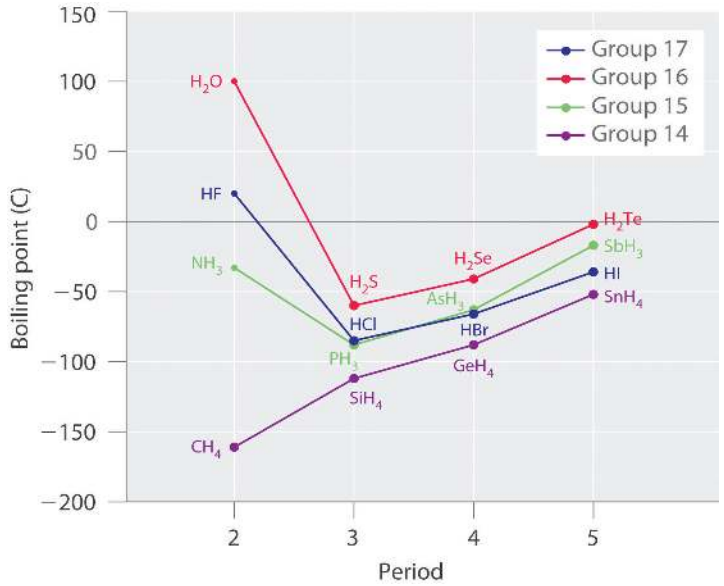


Figure 12.3.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously 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 12.3.6. 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.

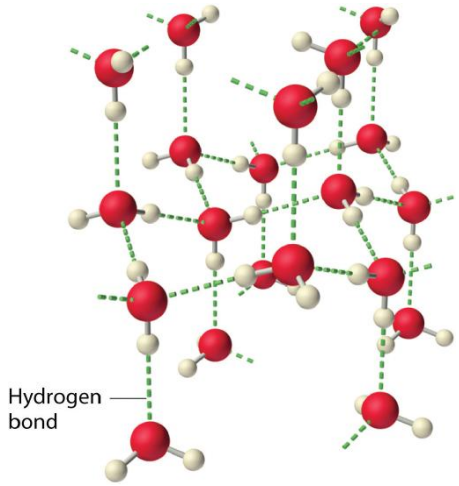
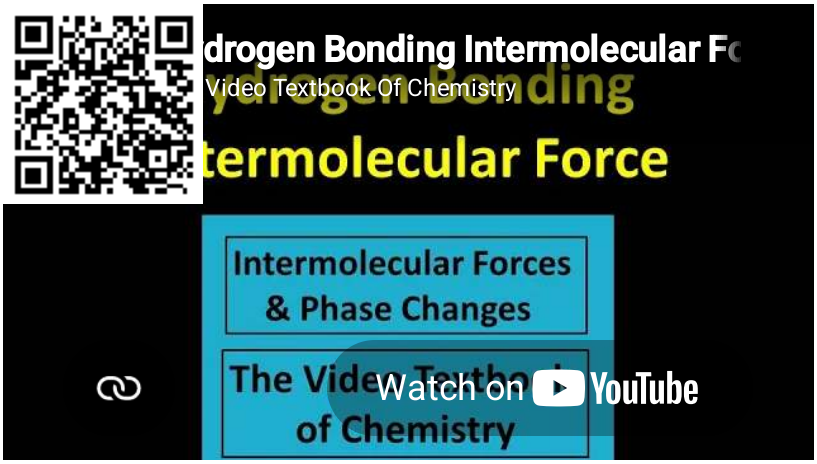


Figure 12.3.6: The Hydrogen-Bonded Structure of Ice

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.



Video Discussing Hydrogen Bonding Intermolecular Forces. Source: Hydrogen Bonding Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 12.3.3

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:

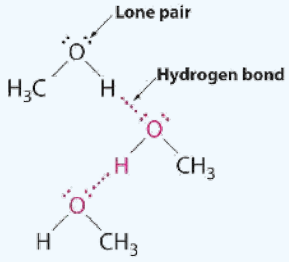
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

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:



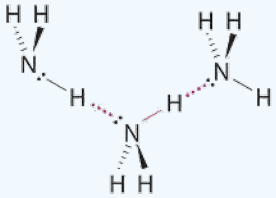
Hydrogen bonding in methanol

Exercise 12.3.3

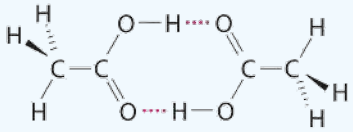
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

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.

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 12.3.4: 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 12.3.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Example 12.3.5

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 12.3.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

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.

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12.4: Intermolecular Forces in Action- Surface Tension, Viscosity, and Capillary Action

Learning Objectives

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions:

- surface tension,
- capillary action, and
- viscosity.

Surface Tension

If liquids tend to adopt the shapes of their containers, then why do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29×10^{-2} J/m^2 (at 20°C), while mercury with metallic bonds has as surface tension that is 15 times higher: 4.86×10^{-1} J/m^2 (at 20°C).

Figure 12.4.1 presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

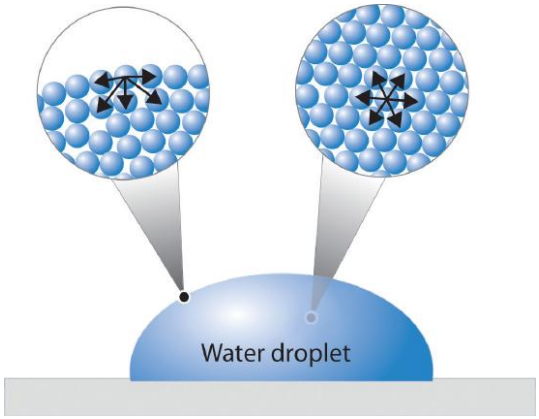


Figure 12.4.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even

observable in the zero gravity conditions of space as shown in Figure 12.4.2 (and more so in the video link) where water wrung from a wet towel continues to float along the towel's surface!



Figure 12.4.2: The Effects of the High Surface Tension of Liquid Water. The full video can be found at www.youtube.com/watch?v=9jB7rOC5kG8.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table 12.4.1. 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 12.4.1: 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.

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 12.4.3. When a glass capillary is is placed in liquid water, water rises up into the capillary. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

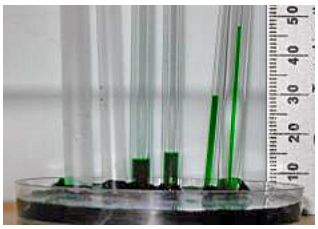


Figure 12.4.3: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

- Cohesive forces bind molecules of the same type together
- Adhesive forces bind a substance to a surface

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (Figure 12.4.4). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure 12.4.4).

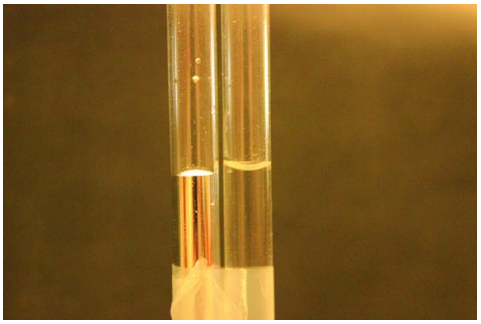


Figure 12.4.4: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

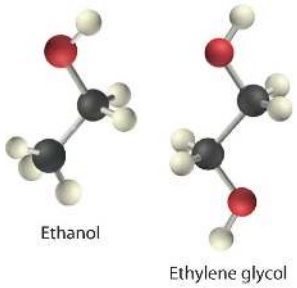
Polar substances are drawn up a glass capillary and generally have a concave meniscus.

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported

from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

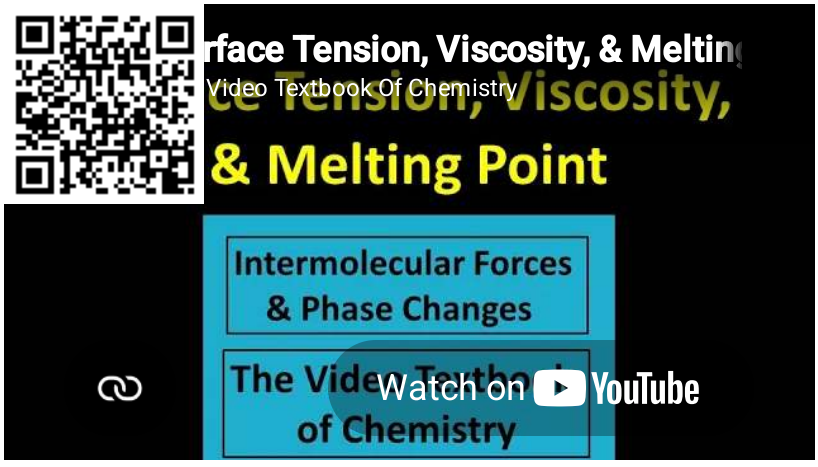
Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*



Video Discussing Surface Tension and Viscosity. Video Link: Surface Tension, Viscosity, & Melting Point, YouTube(opens in new window) [youtu.be]

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.



Figure 12.4.5: Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity (Figure 12.4.5). So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Example 12.4.1

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 12.4.1

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.

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.

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12.5: Vaporization and Vapor Pressure

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (*KE*) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure 12.5.1), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

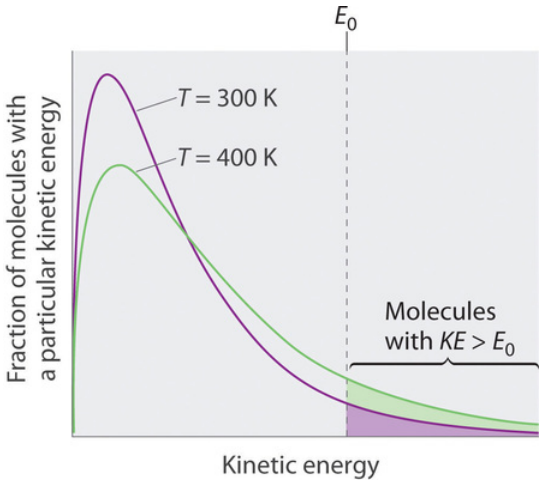


Figure 12.5.1: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

Graph of fraction of molecules with a particular kinetic energy against kinetic energy. Green line is temperature at 400 kelvin, purple line is temperature at 300 kelvin.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 12.5.2. When a liquid is introduced into an evacuated chamber (part (a) in Figure 12.5.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

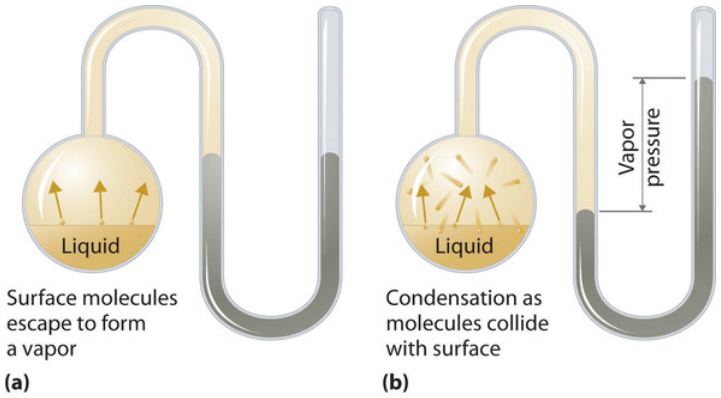


Figure 12.5.2: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure 12.5.2). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 12.5.3.

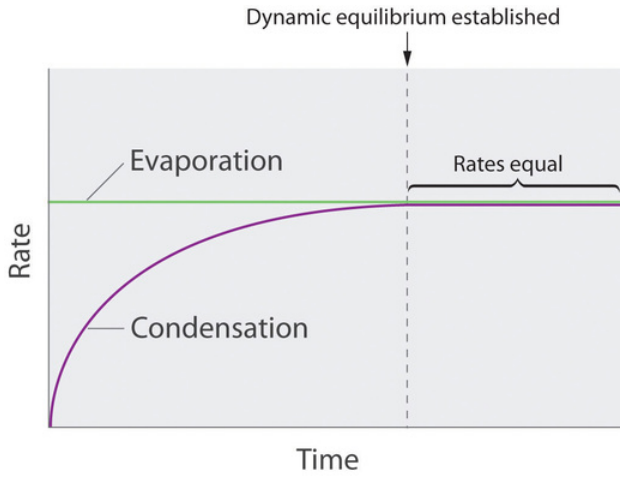


Figure 12.5.3: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

Graph of rate against time. The green line is evaporation while the pruple line is condensation. Dynamic equilibrium is established when the evaporation and condensation rates are equal.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has "disappeared." The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure 12.5.4) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

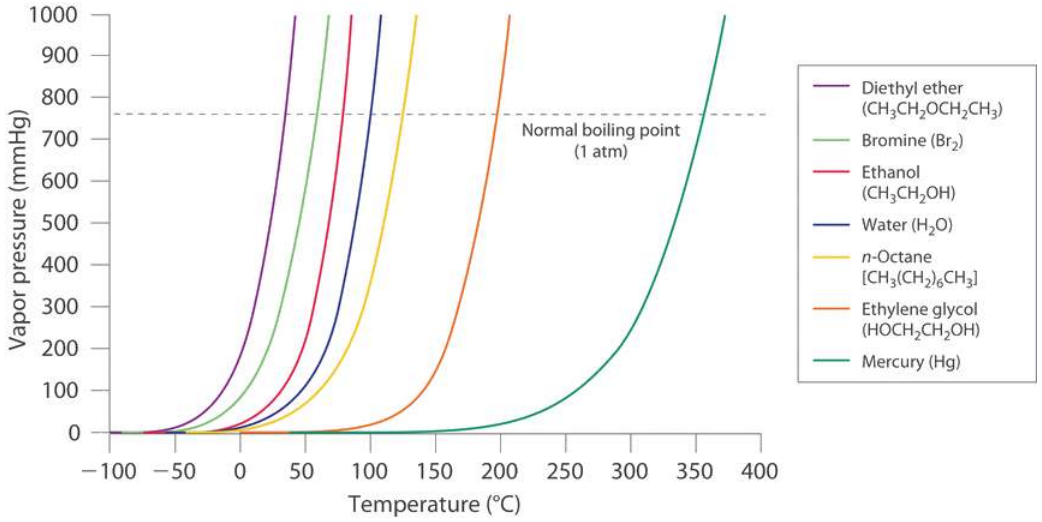
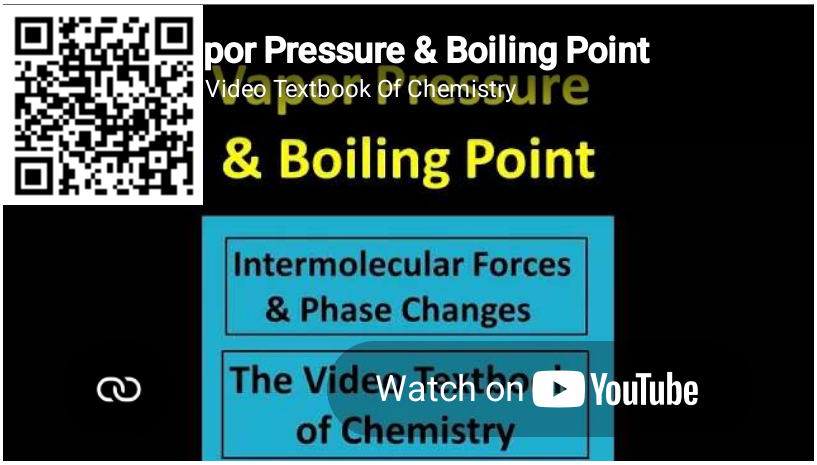


Figure 12.5.4: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 12.5.4. Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*



A Video Discussing Vapor Pressure and Boiling Points. Video Source: Vapor Pressure & Boiling Point(opens in new window) [youtu.be]

The exponential rise in vapor pressure with increasing temperature in Figure 12.5.4 allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$\boxed{\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C} \tag{12.5.1}$$

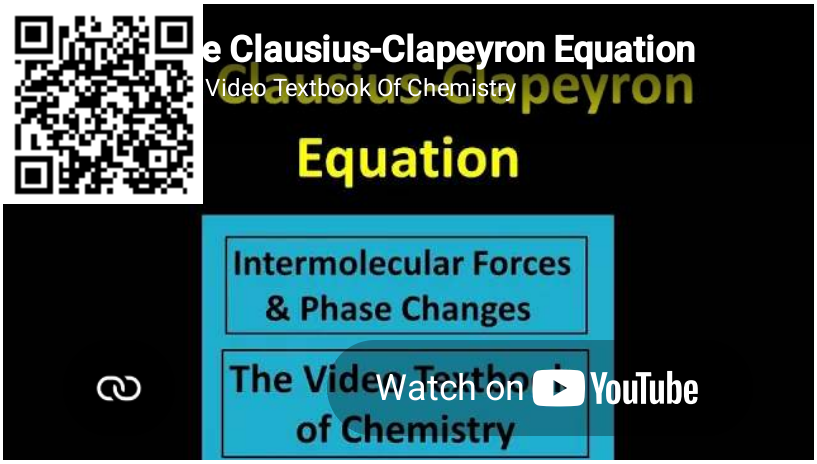
where

- $\ln P$ is the natural logarithm of the vapor pressure,
- ΔH_{vap} is the enthalpy of vaporization,
- R is the universal gas constant [8.314 J/(mol•K)],
- T is the temperature in kelvins, and
- C is the y-intercept, which is a constant for any given line.

Plotting $\ln P$ versus the inverse of the absolute temperature ($1/T$) is a straight line with a slope of $-\Delta H_{\text{vap}}/R$. Equation 12.5.1, called the Clausius–Clapeyron Equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of P and T for these points into Equation 12.5.2, which is derived from the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{12.5.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation 12.5.2 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 12.5.1.



A Video Discussing the Clausius-Clapeyron Equation. Video Link: The Clausius-Clapeyron Equation(opens in new window) [youtu.be]

Example 12.5.1: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

experimentally measured vapor pressures of liquid Hg at four temperatures

T (°C)	80.0	100	120	140
P (torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 12.5.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.

B. Substitute the calculated value of ΔH_{vap} into Equation 12.5.2 to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 12.5.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 12.5.2 to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 12.5.2 gives

$$\ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot K}\left(\frac{1}{(120+273)\ K} - \frac{1}{(80.0+273)\ K}\right)$$

$$\ln(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot \cancel{K}}\left(-2.88 \times 10^{-4}\ \cancel{K^{-1}}\right)$$

$$2.13 = -\Delta H_{vap}\left(-3.46 \times 10^{-4}\right) J^{-1} \cdot mol$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$\ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\ K} - \frac{1}{(80.0+273)\ K}\right)$$

Using the relationship $e^{\ln x} = x$, we have

$$\ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5$$

$$P_2 = 4.21 Torr$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

? Exercise 12.5.1: Vapor Pressure of Nickel

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer

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 12.5.4 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table 12.5.1: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
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 12.5.1 lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

✓ Example 12.5.2: Boiling Mercury

Use Figure 12.5.4 to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C



Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure 12.5.4, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 12.5.4 and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.

B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.

b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise 12.5.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure 12.5.4 to estimate the following.

a. the normal boiling point of ethylene glycol

b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

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12.6: Sublimation and Fusion

Sublimation

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as sublimation. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure 12.6.6). The reverse of sublimation is called deposition, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.



This figure shows a test tube. In the bottom is a dark substance which breaks up into a purple gas at the top.

Figure 12.6.6: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔHsub, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g) \quad \Delta H_{\mathrm{sub}} = 26.1\ \mathrm{kJ/mol} \tag{12.6.1}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO_2}(s) \quad \Delta H_{\mathrm{dep}} = -\Delta H_{\mathrm{sub}} = -26.1\ \mathrm{kJ/mol} \tag{12.6.2}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law.

$$\begin{array}{r} \text{solid} \longrightarrow \text{liquid} \quad \Delta H_{\mathrm{fus}} \\ \underline{\text{liquid} \longrightarrow \text{gas} \quad \Delta H_{\mathrm{vap}}} \\ \text{solid} \longrightarrow \text{gas} \quad \Delta H_{\mathrm{sub}} = \Delta H_{\mathrm{fus}} + \Delta H_{\mathrm{vap}} \end{array} \tag{12.6.3}$$

Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 12.6.7. For example:

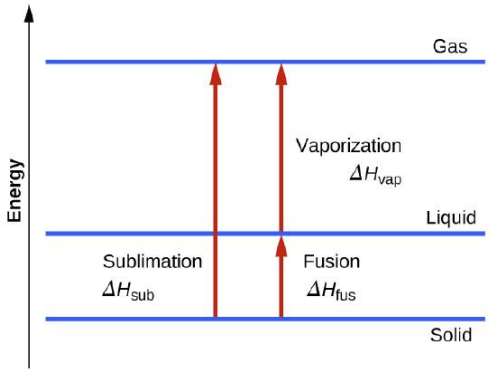


Figure 12.6.7*: For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.*

An energy level diagram is shown with three horizontal lines representing states of solid, liquid, and gas in increasing energy levels. The enthalpy of fusion is shown by arrow pointing from solid to liquid. Enthalpy of vaporization is shown with arrow pointing from liquid to gas. The enthalpy of sublimation points from solid to gas and has the same length as the arrows for fusion and vaporization combined.

Fusion

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure \(\PageIndex{5}\).



Figure 12.6.5: (a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott).

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal process of melting and freezing occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the melting point of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \Delta H_{\text{fus}} = 6.01 \text{ kJ/mol} \tag{12.6.4}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$H_2O_{(l)} \rightarrow H_2O_{(s)} \quad \Delta H_{\text{frz}} = -\Delta H_{\text{fus}} = -6.01 \text{ kJ/mol} \tag{12.6.5}$$

Selected molar enthalpies of fusion are tabulated in Table 12.6.1. Solids like ice which have strong intermolecular forces have much higher values than those like CH_4 with weak ones. Note that the enthalpies of fusion and vaporization change with temperature.

Table 12.6.1: Molar Enthalpies of Fusion and Vaporization of Selected Substances.

Substance	Formula	ΔH(fusion) / kJ mol^1	Melting Point / K	ΔH(vaporization) / kJ mol^{-1}	Boiling Point / K	($\Delta H_v/T_b$) / JK^{-1} mol^{-1}
Neon	Ne	0.33	24	1.80	27	67
Oxygen	O_2	0.44	54	6.82	90.2	76
Methane	CH_4	0.94	90.7	8.18	112	73
Ethane	C_2H_6	2.85	90.0	14.72	184	80
Chlorine	Cl_2	6.40	172.2	20.41	239	85
Carbon tetrachloride	CCl_4	2.67	250.0	30.00	350	86
Water*	H_2O	6.00678 at 0°C, 101kPa 6.354 at 81.6 °C, 2.50 MPa	273.1	40.657 at 100 °C, 45.051 at 0 °C, 46.567 at -33 °C	373.1	109
n-Nonane	C_9H_{20}	19.3	353	40.5	491	82
Mercury	Hg	2.30	234	58.6	630	91
Sodium	Na	2.60	371	98	1158	85
Aluminum	Al	10.9	933	284	2600	109
Lead	Pb	4.77	601	178	2022	88

*www1.lsbu.ac.uk/water/data.html

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12.7: Heating Curve for Water

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 12.7.3 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.

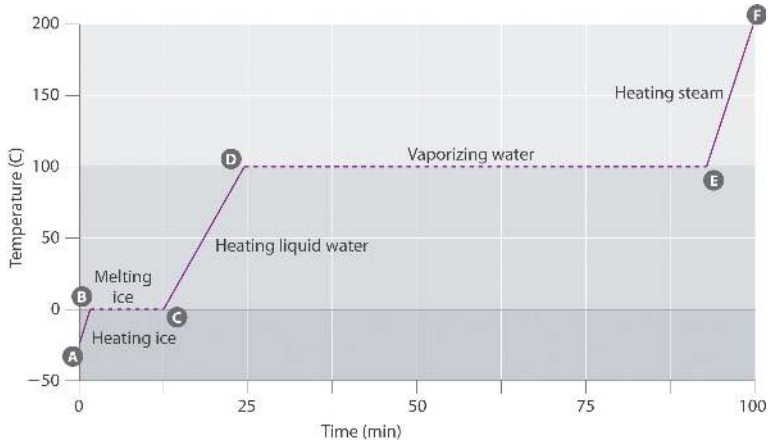


Figure 12.7.1: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

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 12.7.3, 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 12.7.3, 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 12.7.4 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 12.7.3, 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.

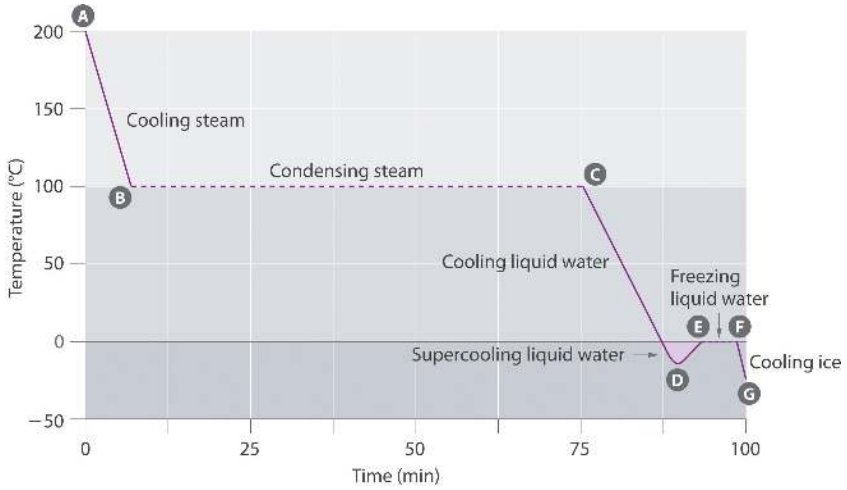


Figure 12.7.2: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid 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 12.7.1: 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

$$q = mC_s\Delta T \tag{12.7.1}$$

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 12.7.1: 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 12.7.1

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.

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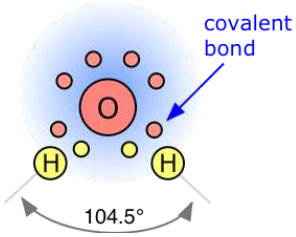
12.8: Water - An Extraordinary Substance

Learning Objectives

- Identify three special properties of water that make it unusual for a molecule of its size, and explain how these result from hydrogen bonding.
- Explain what is meant by hydrogen bonding and the molecular structural features that bring it about.
- Describe the "structure", such as it is, of liquid water.
- Sketch out structural examples of hydrogen bonding in three small molecules other than H_2O.
- Describe the roles of hydrogen bonding in proteins and in DNA.

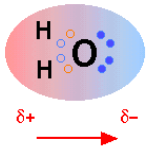
Most students of chemistry quickly learn to relate the structure of a molecule to its general properties. Thus we generally expect small molecules to form gases or liquids, and large ones to exist as solids under ordinary conditions. And then we come to H_2O, and are shocked to find that many of the predictions are way off, and that water (and by implication, life itself) should not even exist on our planet! In this section we will learn why this tiny combination of three nuclei and ten electrons possesses special properties that make it unique among the more than 15 million chemical species we presently know.

In water, each hydrogen nucleus is covalently bound to the central oxygen atom by a pair of electrons that are shared between them. In H_2O, only two of the six outer-shell electrons of oxygen are used for this purpose, leaving four electrons which are organized into two non-bonding pairs. The four electron pairs surrounding the oxygen tend to arrange themselves as far from each other as possible in order to minimize repulsions between these clouds of negative charge. This would ordinarily result in a tetrahedral geometry in which the angle between electron pairs (and therefore the H-O-H *bond angle*) is 109.5°. However, because the two non-bonding pairs remain closer to the oxygen atom, these exert a stronger repulsion against the two covalent bonding pairs, effectively pushing the two hydrogen atoms closer together. The result is a distorted tetrahedral arrangement in which the H—O—H angle is 104.5°.

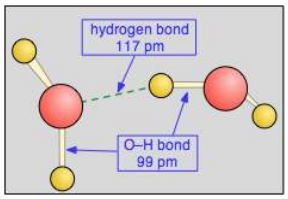


Water's large dipole moment leads to hydrogen bonding

The H_2O molecule is electrically neutral, but the positive and negative charges are not distributed uniformly. This is illustrated by the gradation in color in the schematic diagram here. The electronic (negative) charge is concentrated at the oxygen end of the molecule, owing partly to the nonbonding electrons (solid blue circles), and to oxygen's high nuclear charge which exerts stronger attractions on the electrons. This charge displacement constitutes an *electric dipole*, represented by the arrow at the bottom; you can think of this dipole as the electrical "image" of a water molecule.

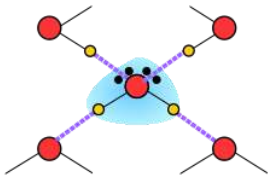


Opposite charges attract, so it is not surprising that the negative end of one water molecule will tend to orient itself so as to be close to the positive end of another molecule that happens to be nearby. The strength of this *dipole-dipole attraction* is less than that of a normal chemical bond, and so it is completely overwhelmed by ordinary thermal motions in the gas phase. However, when the H_2O molecules are crowded together in the liquid, these attractive forces exert a very noticeable effect, which we call (somewhat misleadingly) *hydrogen bonding*. And at temperatures low enough to turn off the disruptive effects of thermal motions, water freezes into ice in which the hydrogen bonds form a rigid and stable network.



Notice that the hydrogen bond (shown by the dashed green line) is somewhat longer than the covalent O—H bond. It is also *much weaker*, about 23 kJ mol^{-1} compared to the O–H covalent bond strength of 492 kJ mol^{-1}.

Water has long been known to exhibit many physical properties that distinguish it from other small molecules of comparable mass. Although chemists refer to these as the "anomalous" properties of water, they are by no means mysterious; all are entirely predictable consequences of the way the size and nuclear charge of the oxygen atom conspire to distort the electronic charge clouds of the atoms of other elements when these are chemically bonded to the oxygen.



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 12.8.6. 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.

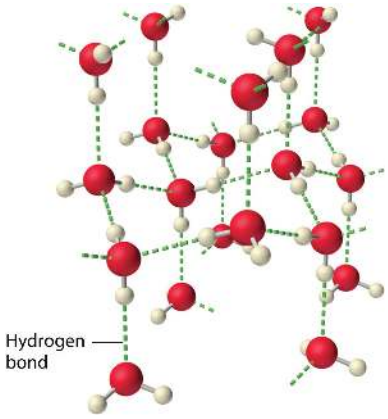


Figure 12.8.6***:*** *The Hydrogen-Bonded Structure of Ice.*

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, cagelike 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.*

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 12.8.5. 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.

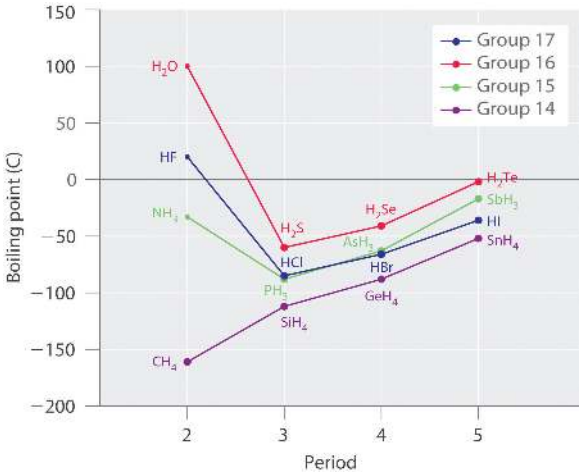
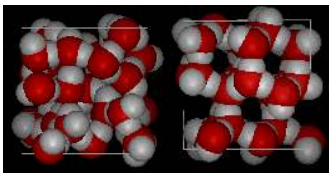


Figure 12.8.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

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.

Ice Floats on Water

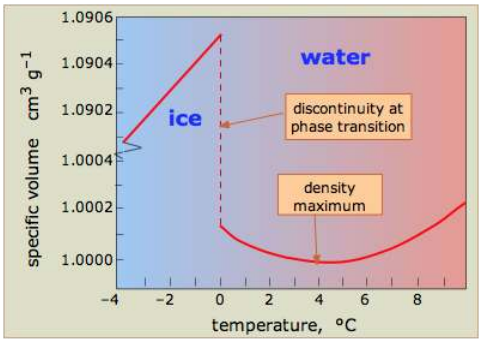
The most energetically favorable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighboring molecules. Owing to the thermal motions described above, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart then would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.



Here are three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of hydrogen bonding in a uniform, extended crystal lattice. The more

crowded and jumbled arrangement in liquid water can be sustained only by the greater amount of thermal energy available above the freezing point.

When ice melts, the more vigorous thermal motion disrupts much of the hydrogen-bonded structure, allowing the molecules to pack more closely. Water is thus one of the very few substances whose solid form has a lower density than the liquid at the freezing point. Localized clusters of hydrogen bonds still remain, however; these are continually breaking and reforming as the thermal motions jiggle and shove the individual molecules. As the temperature of the water is raised above freezing, the extent and lifetimes of these clusters diminish, so the density of the water increases.



At higher temperatures, another effect, common to all substances, begins to dominate: as the temperature increases, so does the amplitude of thermal motions. This more vigorous jostling causes the average distance between the molecules to increase, reducing the density of the liquid; this is ordinary thermal expansion. Because the two competing effects (hydrogen bonding at low temperatures and thermal expansion at higher temperatures) both lead to a decrease in density, it follows that there must be some temperature at which the density of water passes through a maximum. This temperature is 4° C; this is the temperature of the water you will find at the bottom of an ice-covered lake in which this most dense of all water has displaced the colder water and pushed it nearer to the surface.

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.

Contributors

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CHAPTER OVERVIEW

13: Phase Diagrams and Crystalline Solids

13.1: Sliding Glaciers
13.2: Phase Diagrams
13.3: Crystalline Solids- Determining Their Structure by X-Ray Crystallography
13.4: Crystalline Solids- Unit Cells and Basic Structures
13.5: Crystalline Solids- The Fundamental Types
13.6: The Structure of Ionic Solids
13.7: Network Covalent Atomic Solids- Carbon and Silicates

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13.1: Sliding Glaciers



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13.2: 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 13.2.1). 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 13.2.1) 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.

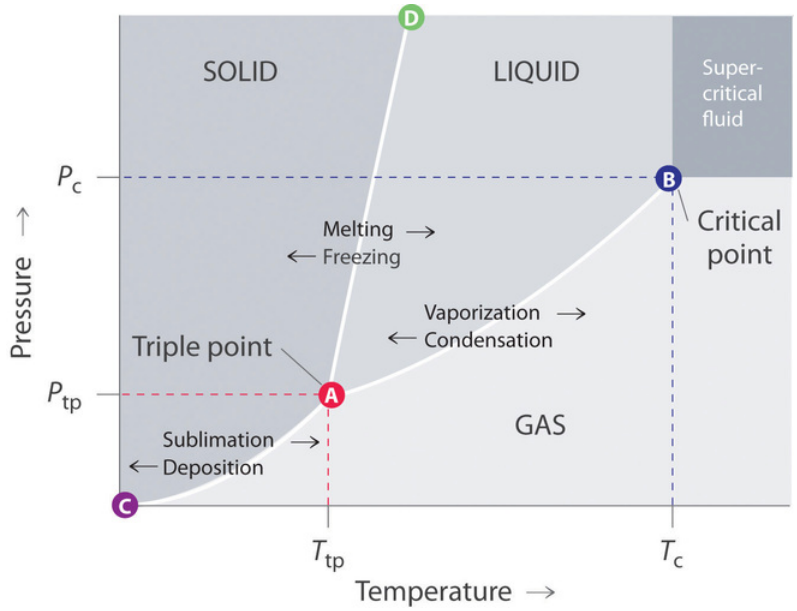


Figure 13.2.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

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 13.2.1, 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 13.2.1, 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 13.2.2 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).

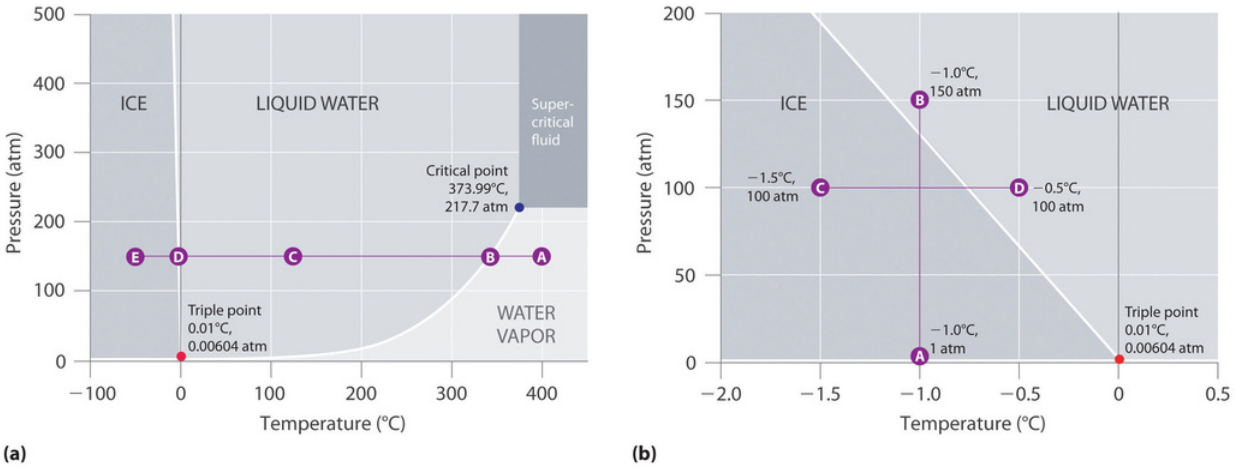


Figure 13.2.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 13.2.1).

The phase diagram for water illustrated in Figure 13.2.2*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 13.2.1; 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 13.2.2*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 13.2.1: Water

Referring to the phase diagram of water in Figure 13.2.2:

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 13.2.2. 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 13.2.2. 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 13.2.2

Referring to the phase diagram of water in Figure 13.2.2, 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

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.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure 13.2.3) 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.

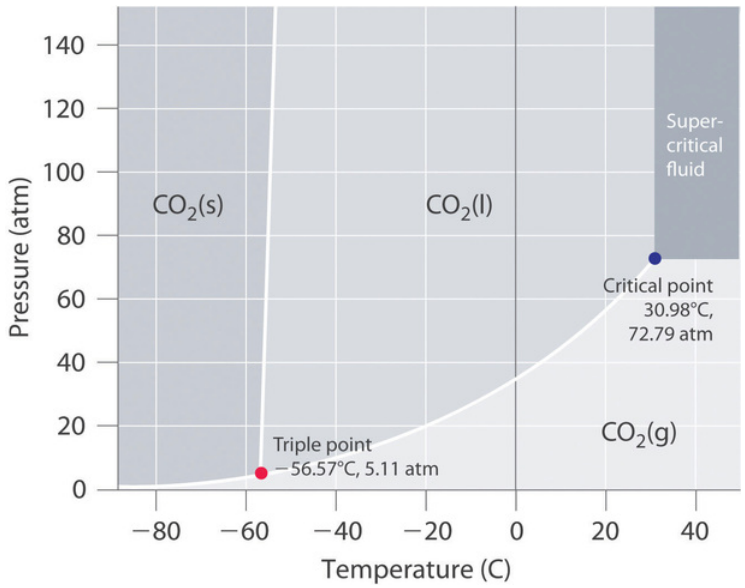


Figure 13.2.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

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.

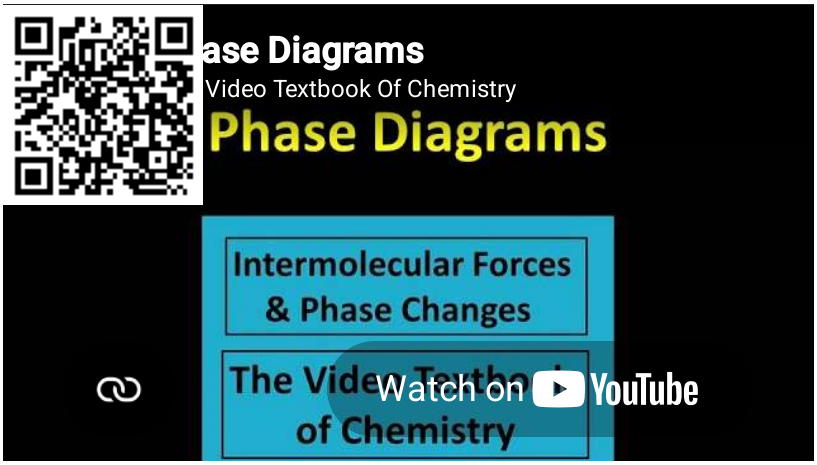
The Critical Point

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 13.2.1.

Figure 13.2.1: 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.



A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

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13.3: Crystalline Solids- Determining Their Structure by X-Ray Crystallography

Learning Objectives

By the end of this section, you will be able to:

- Describe interference and diffraction effects exhibited by X-rays in interaction with atomic-scale structures

Since X-ray photons are very energetic, they have relatively short wavelengths, on the order of 10^{-8} m to 10^{-12} m. Thus, typical X-ray photons act like rays when they encounter macroscopic objects, like teeth, and produce sharp shadows. However, since atoms are on the order of 0.1 nm in size, X-rays can be used to detect the location, shape, and size of atoms and molecules. The process is called **X-ray diffraction**, and it involves the interference of X-rays to produce patterns that can be analyzed for information about the structures that scattered the X-rays.

Perhaps the most famous example of X-ray diffraction is the discovery of the double-helical structure of **DNA** in 1953 by an international team of scientists working at England's Cavendish Laboratory—American James Watson, Englishman Francis Crick, and New Zealand-born Maurice Wilkins. Using X-ray diffraction data produced by Rosalind Franklin, they were the first to model the double-helix structure of DNA that is so crucial to life. For this work, Watson, Crick, and Wilkins were awarded the 1962 Nobel Prize in Physiology or Medicine. (There is some debate and controversy over the issue that Rosalind Franklin was not included in the prize, although she died in 1958, before the prize was awarded.)

Figure 13.3.1 shows a diffraction pattern produced by the scattering of X-rays from a crystal. This process is known as X-ray crystallography because of the information it can yield about crystal structure, and it was the type of data Rosalind Franklin supplied to Watson and Crick for DNA. Not only do X-rays confirm the size and shape of atoms, they give information about the atomic arrangements in materials. For example, more recent research in high-temperature superconductors involves complex materials whose lattice arrangements are crucial to obtaining a superconducting material. These can be studied using X-ray crystallography.

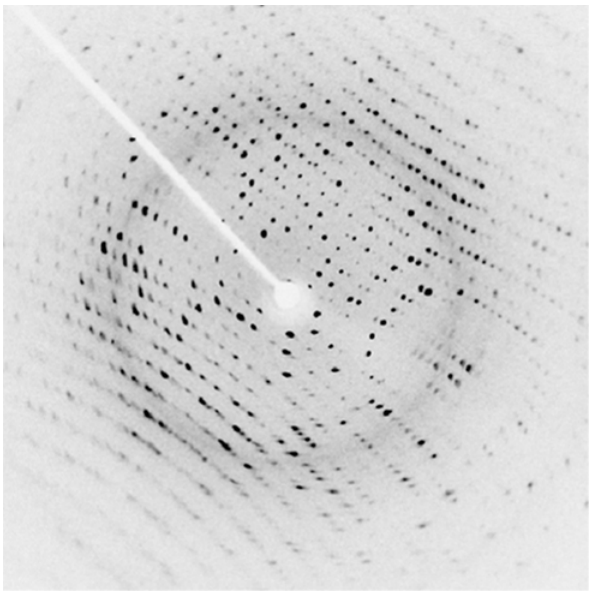


Figure 13.3.1: X-ray diffraction from the crystal of a protein (hen egg lysozyme) produced this interference pattern. Analysis of the pattern yields information about the structure of the protein. (credit: "Del45"/Wikimedia Commons)

Historically, the scattering of X-rays from crystals was used to prove that X-rays are energetic electromagnetic (EM) waves. This was suspected from the time of the discovery of X-rays in 1895, but it was not until 1912 that the German Max **von Laue** (1879–1960) convinced two of his colleagues to scatter X-rays from crystals. If a diffraction pattern is obtained, he reasoned, then the X-rays must be waves, and their wavelength could be determined. (The spacing of atoms in various crystals was reasonably well known at the time, based on good values for Avogadro's number.) The experiments were convincing, and the 1914 Nobel Prize in

Physics was given to von Laue for his suggestion leading to the proof that X-rays are EM waves. In 1915, the unique father-and-son team of Sir William Henry **Bragg** and his son Sir William Lawrence Bragg were awarded a joint Nobel Prize for inventing the X-ray spectrometer and the then-new science of X-ray analysis.

In ways reminiscent of thin-film interference, we consider two plane waves at X-ray wavelengths, each one reflecting off a different plane of atoms within a crystal's lattice, as shown in Figure 13.3.2. From the geometry, the difference in path lengths is $2d \sin \theta$. Constructive interference results when this distance is an integer multiple of the wavelength. This condition is captured by the **Bragg equation**,

$$m\lambda = 2d \sin \theta, \tag{13.3.1}$$

for $m = 1, 2, 3, ...$

where m is a positive integer and d is the spacing between the planes. Following the Law of Reflection, both the incident and reflected waves are described by the same angle, θ, but unlike the general practice in geometric optics, θ is measured with respect to the surface itself, rather than the normal.

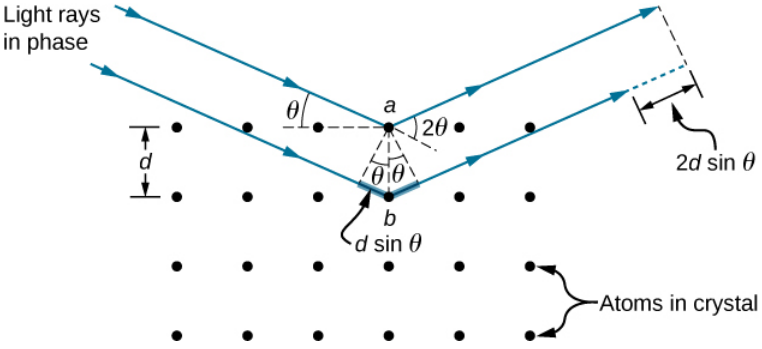


Figure 13.3.2: X-ray diffraction with a crystal. Two incident waves reflect off two planes of a crystal. The difference in path lengths is indicated by the dashed line.

Example 13.3.1: X-Ray Diffraction with Salt Crystals

Common table salt is composed mainly of NaCl crystals. In a NaCl crystal, there is a family of planes 0.252 nm apart. If the first-order maximum is observed at an incidence angle of 18.1°, what is the wavelength of the X-ray scattering from this crystal?

Strategy:

Use the Bragg equation, Equation 13.3.1, to solve for θ.

Solution

For first-order, $m = 1$, and the plane spacing d is known. Solving the Bragg equation for wavelength yields

$$\begin{aligned} \lambda &= \frac{2d \sin \theta}{m} \\ &= \frac{2(0.252 \times 10^{-9} m) \sin (18.1^{o})}{1} \\ &= 1.57 \times 10^{-10} m, \, or \, 0.157 \, nm \end{aligned}$$

Significance

The determined wavelength fits within the X-ray region of the electromagnetic spectrum. Once again, the wave nature of light makes itself prominent when the wavelength ($\lambda = 0.157 \, nm$) is comparable to the size of the physical structures ($d = 0.252 \, nm$) it interacts with.

? Exercise 13.3.1

For the experiment described in Example 13.3.1, what are the two other angles where interference maxima may be observed? What limits the number of maxima?

Answer

38.4^o and 68.8^o; Between $\theta = 0^o \rightarrow 90^o$, orders 1, 2, and 3, are all that exist.

Although Figure 13.3.2 depicts a crystal as a two-dimensional array of scattering centers for simplicity, real crystals are structures in three dimensions. Scattering can occur simultaneously from different families of planes at different orientations and spacing patterns known as called **Bragg planes**, as shown in Figure 13.3.3. The resulting interference pattern can be quite complex.

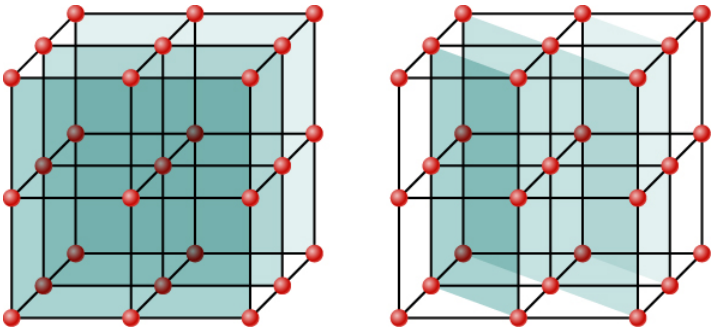


Figure 13.3.3: Because of the regularity that makes a crystal structure, one crystal can have many families of planes within its geometry, each one giving rise to X-ray diffraction.

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13.4: Crystalline Solids- Unit Cells and Basic Structures

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- The difference between square and hexagonal packing in two dimensions.
- The definition and significance of the unit cell.
- Sketch the three Bravais lattices of the cubic system, and calculate the number of atoms contained in each of these unit cells.
- Show how alternative ways of stacking three close-packed layers can lead to the hexagonal or cubic close packed structures.
- Explain the origin and significance of octahedral and tetrahedral holes in stacked close-packed layers, and show how they can arise.

Close-Packing of Identical Spheres

Crystals are of course three-dimensional objects, but we will begin by exploring the properties of arrays in two-dimensional space. This will make it easier to develop some of the basic ideas without the added complication of getting you to visualize in 3-D — something that often requires a bit of practice. Suppose you have a dozen or so marbles. How can you arrange them in a single compact layer on a table top? Obviously, they must be in contact with each other in order to minimize the area they cover. It turns out that there are two efficient ways of achieving this:



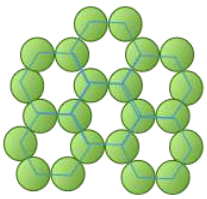
The essential difference here is that any marble within the interior of the square-packed array is in contact with four other marbles, while this number rises to six in the hexagonal-packed arrangement. It should also be apparent that the latter scheme covers a smaller area (contains less empty space) and is therefore a more efficient packing arrangement. If you are good at geometry, you can show that square packing covers 78 percent of the area, while hexagonal packing yields 91 percent coverage.

If we go from the world of marbles to that of atoms, which kind of packing would the atoms of a given element prefer?



If the atoms are identical and are bound together mainly by dispersion forces which are completely non-directional, they will favor a structure in which as many atoms can be in direct contact as possible. This will, of course, be the hexagonal arrangement.

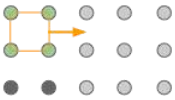
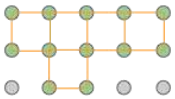
Directed chemical bonds between atoms have a major effect on the packing. The version of hexagonal packing shown at the right occurs in the form of carbon known as *graphite* which forms 2-dimensional sheets. Each carbon atom within a sheet is bonded to three other carbon atoms. The result is just the basic hexagonal structure with some atoms missing.



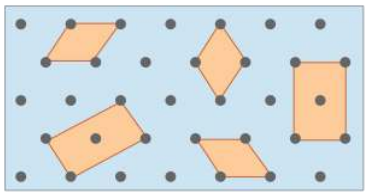
The coordination number of 3 reflects the sp^2-hybridization of carbon in graphite, resulting in plane-trigonal bonding and thus the sheet structure. Adjacent sheets are bound by weak dispersion forces, allowing the sheets to slip over one another and giving rise to the lubricating and flaking properties of graphite.

Lattices

The underlying order of a crystalline solid can be represented by an array of regularly spaced points that indicate the locations of the crystal's basic structural units. This array is called a crystal lattice. Crystal lattices can be thought of as being built up from repeating units containing just a few atoms. These repeating units act much as a rubber stamp: press it on the paper, move ("translate") it by an amount equal to the lattice spacing, and stamp the paper again.

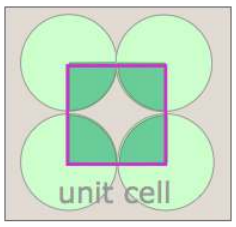
 The gray circles represent a square array of lattice points.	 The orange square is the simplest unit cell that can be used to define the 2-dimensional lattice.	 Building out the lattice by moving ("translating") the unit cell in a series of steps,

Although real crystals do not actually grow in this manner, this process is conceptually important because it allows us to classify a lattice type in terms of the simple repeating unit that is used to "build" it. We call this shape the *unit cell*. Any number of primitive shapes can be used to define the unit cell of a given crystal lattice. The one that is actually used is largely a matter of convenience, and it may contain a lattice point in its center, as you see in two of the unit cells shown here. In general, the best unit cell is the simplest one that is capable of building out the lattice.

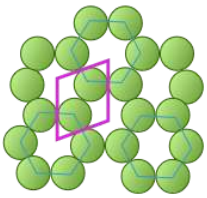




Shown above are unit cells for the close-packed square and hexagonal lattices we discussed near the start of this lesson. Although we could use a hexagon for the second of these lattices, the rhombus is preferred because it is simpler.



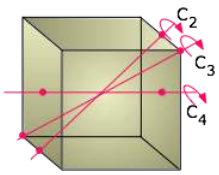
Notice that in both of these lattices, the corners of the unit cells are centered on a lattice point. This means that an atom or molecule located on this point in a real crystal lattice is shared with its neighboring cells. As is shown more clearly here for a two-dimensional square-packed lattice, a single unit cell can claim "ownership" of only one-quarter of each molecule, and thus "contains" 4 × ¼ = 1 molecule.



The unit cell of the graphite form of carbon is also a rhombus, in keeping with the hexagonal symmetry of this arrangement. Notice that to generate this structure from the unit cell, we need to shift the cell in both the *x*- and *y*- directions in order to leave empty spaces at the correct spots. We could alternatively use regular hexagons as the unit cells, but the *x*+*y* shifts would still be required, so the simpler rhombus is usually preferred. As you will see in the next section, the empty spaces within these unit cells play an important role when we move from two- to three-dimensional lattices.

Cubic crystals

In order to keep this lesson within reasonable bounds, we are limiting it mostly to crystals belonging to the so-called *cubic* system. In doing so, we can develop the major concepts that are useful for understanding more complicated structures (as if there are not enough complications in cubics alone!) But in addition, it happens that cubic crystals are very commonly encountered; most metallic elements have cubic structures, and so does ordinary salt, sodium chloride.

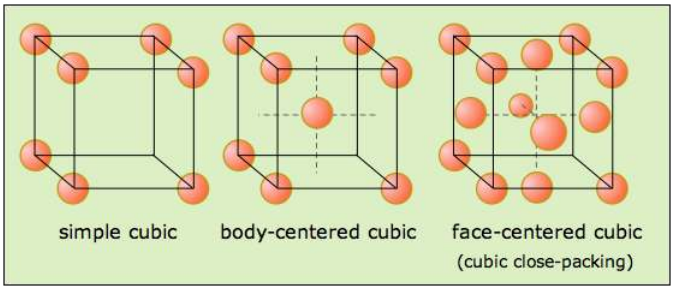


We usually think of a cubic shape in terms of the equality of its edge lengths and the 90° angles between its sides, but there is another way of classifying shapes that chemists find very useful. This is to look at what *geometric transformations* (such as rotations around an axis) we can perform that leave the appearance unchanged. For example, you can rotate a cube 90° around an axis perpendicular to any pair of its six faces without making any apparent change to it. We say that the cube possesses three mutually perpendicular *four-fold rotational axes*, abbreviated C_4 axes. But if you think about it, a cube can also be rotated around the axes that extend between opposite corners; in this case, it takes three 120° rotations to go through a complete circle, so these axes (also four in number) are three-fold or C_3 axes.

Cubic crystals belong to one of the seven crystal systems whose lattice points can be extended indefinitely to fill three-dimensional space and which can be constructed by successive translations (movements) of a primitive unit cell in three dimensions. As we will see below, the cubic system, as well as some of the others, can have variants in which additional lattice points can be placed at the center of the unit or at the center of each face.

The three types of cubic lattices

The three Bravais lattices which form the cubic crystal system are shown here.



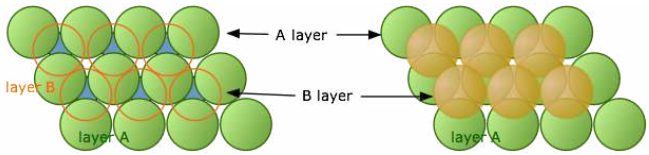
Structural examples of all three are known, with body- and face-centered (BCC and FCC) being much more common; most metallic elements crystallize in one of these latter forms. But although the simple cubic structure is uncommon by itself, it turns out that many BCC and FCC structures composed of ions can be regarded as interpenetrating combinations of two simple cubic

lattices, one made up of positive ions and the other of negative ions. Notice that only the FCC structure, which we will describe below, is a close-packed lattice within the cubic system.

Close-packed lattices in three dimensions

Close-packed lattices allow the maximum amount of interaction between atoms. If these interactions are mainly attractive, then close-packing usually leads to more energetically stable structures. These lattice geometries are widely seen in metallic, atomic, and simple ionic crystals.

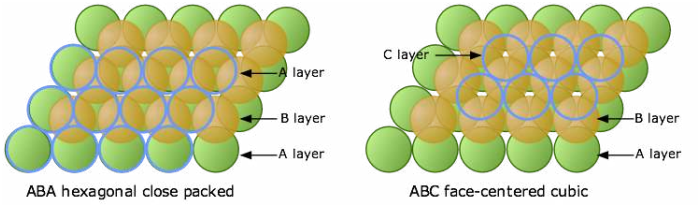
As we pointed out above, hexagonal packing of a single layer is more efficient than square-packing, so this is where we begin. Imagine that we start with the single layer of green atoms shown below. We will call this the A layer. If we place a second layer of atoms (orange) on top of the A-layer, we would expect the atoms of the new layer to nestle in the hollows in the first layer. But if all the atoms are identical, only some of these void spaces will be accessible.



In the diagram on the left, notice that there are two classes of void spaces between the A atoms; one set (colored blue) has a vertex pointing up, while the other set (not colored) has down-pointing vertices. Each void space constitutes a depression in which atoms of a second layer (the B-layer) can nest. The two sets of void spaces are completely equivalent, but only one of these sets can be occupied by a second layer of atoms whose size is similar to those in the bottom layer. In the illustration on the right above we have arbitrarily placed the B-layer atoms in the blue voids, but could just as well have selected the white ones.

Two choices for the third layer lead to two different close-packed lattice types

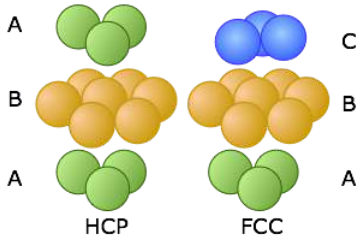
Now consider what happens when we lay down a third layer of atoms. These will fit into the void spaces within the B-layer. As before, there are two sets of these positions, but unlike the case described above, they are not equivalent.



The atoms in the third layer are represented by open blue circles in order to avoid obscuring the layers underneath. In the illustration on the left, this third layer is placed on the B-layer at locations that are directly above the atoms of the A-layer, so our third layer is just a another A layer. If we add still more layers, the vertical sequence A-B-A-B-A-B-A... repeats indefinitely.

In the diagram on the right above, the blue atoms have been placed above the white (unoccupied) void spaces in layer A. Because this third layer is displaced horizontally (in our view) from layer A, we will call it layer C. As we add more layers of atoms, the sequence of layers is A-B-C-A-B-C-A-B-C..., so we call it ABC packing.

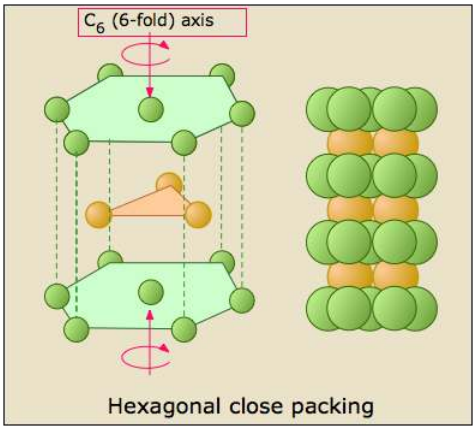
> For the purposes of clarity, only three atoms of the A and C layers are shown in these diagrams. But in reality, each layer consists of an extended hexagonal array; the two layers are simply displaced from one another.



These two diagrams that show exploded views of the vertical stacking further illustrate the rather small fundamental difference between these two arrangements— but, as you will see below, they have widely divergent structural consequences. Note the opposite orientations of the A and C layers

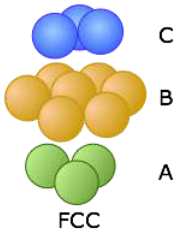
The Hexagonal closed-packed structure

The HCP stacking shown on the left just above takes us out of the cubic crystal system into the hexagonal system, so we will not say much more about it here except to point out each atom has 12 nearest neighbors: six in its own layer, and three in each layer above and below it.

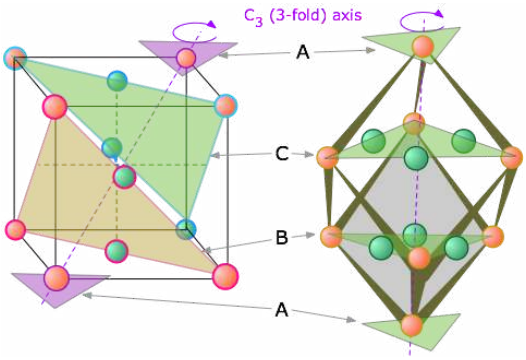


The cubic close-packed structure

Below we reproduce the FCC structure that was shown above.



You will notice that the B-layer atoms form a hexagon, but this is a *cubic* structure. How can this be? The answer is that the FCC stack is inclined with respect to the faces of the cube, and is in fact coincident with one of the three-fold axes that passes through opposite corners. It requires a bit of study to see the relationship, and we have provided two views to help you. The one on the left shows the cube in the normal isometric projection; the one on the right looks down upon the top of the cube at a slightly inclined angle.

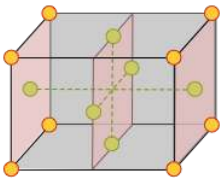


Both the CCP and HCP structures fill 74 percent of the available space when the atoms have the same size. You should see that the two shaded planes cutting along diagonals within the interior of the cube contain atoms of different colors, meaning that they

belong to different layers of the CCP stack. Each plane contains three atoms from the B layer and three from the C layer, thus reducing the symmetry to C_3, which a cubic lattice must have.

The FCC unit cell

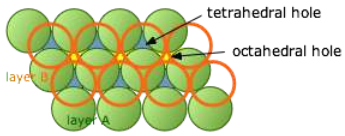
The figure below shows the the face-centered cubic unit cell of a cubic-close packed lattice.



How many atoms are contained in a unit cell? Each corner atom is shared with eight adjacent unit cells and so a single unit cell can claim only 1/8 of each of the eight corner atoms. Similarly, each of the six atoms centered on a face is only half-owned by the cell. The grand total is then (8 × 1/8) + (6 × ½) = 4 atoms per unit cell.

Interstitial Void Spaces

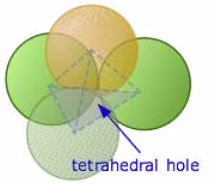
The atoms in each layer in these close-packing stacks sit in a depression in the layer below it. As we explained above, these void spaces are not completely filled. (It is geometrically impossible for more than two identical spheres to be in contact at a single point.) We will see later that these *interstitial void spaces* can sometimes accommodate additional (but generally smaller) atoms or ions.



If we look down on top of two layers of close-packed spheres, we can pick out two classes of void spaces which we call *tetrahedral* and *octahedral holes*.

Tetrahedral holes

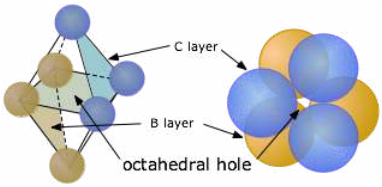
If we direct our attention to a region in the above diagram where a single atom is in contact with the three atoms in the layers directly below it, the void space is known as a *tetrahedral hole*. A similar space will be be found between this single atom and the three atoms (not shown) that would lie on top of it in an extended lattice. Any interstitial atom that might occupy this site will interact with the four atoms surrounding it, so this is also called a *four-coordinate interstitial space*.



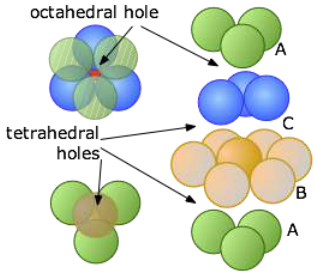
Don't be misled by this name; the boundaries of the void space are spherical sections, not tetrahedra. The tetrahedron is just an imaginary construction whose four corners point to the centers of the four atoms that are in contact.

Octahedral holes

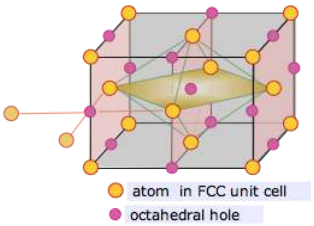
Similarly, when two sets of three trigonally-oriented spheres are in close-packed contact, they will be oriented 60° apart and the centers of the spheres will define the six corners of an imaginary octahedron centered in the void space between the two layers, so we call these *octahedral holes* or *six-coordinate interstitial sites*. Octahedral sites are larger than tetrahedral sites.



An octahedron has six corners and eight sides. We usually draw octahedra as a double square pyramid standing on one corner (left), but in order to visualize the octahedral shape in a close-packed lattice, it is better to think of the octahedron as lying on one of its faces (right).



Each sphere in a close-packed lattice is associated with one octahedral site, whereas there are only half as many tetrahedral sites. This can be seen in this diagram that shows the central atom in the B layer in alignment with the hollows in the C and A layers above and below.



The face-centered cubic unit cell contains a single octahedral hole within itself, but octahedral holes shared with adjacent cells exist at the centers of each edge. Each of these twelve edge-located sites is shared with four adjacent cells, and thus contributes (12 × ¼) = 3 atoms to the cell. Added to the single hole contained in the middle of the cell, this makes a total of 4 octahedral sites per unit cell. This is the same as the number we calculated above for the number of atoms in the cell.

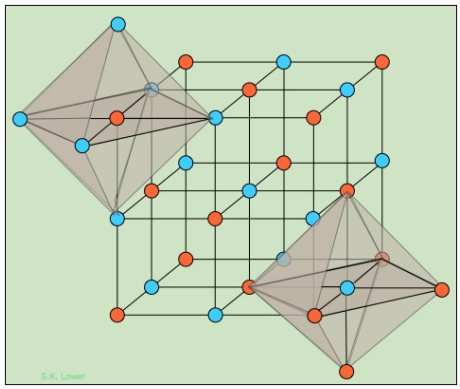
Common cubic close-packed structures

It can be shown from elementary trigonometry that an atom will fit exactly into an octahedral site if its radius is 0.414 as great as that of the host atoms. The corresponding figure for the smaller tetrahedral holes is 0.225.

Many pure metals and compounds form face-centered cubic (cubic close- packed) structures. The existence of tetrahedral and octahedral holes in these lattices presents an opportunity for "foreign" atoms to occupy some or all of these interstitial sites. In order to retain close-packing, the interstitial atoms must be small enough to fit into these holes without disrupting the host CCP lattice. When these atoms are too large, which is commonly the case in ionic compounds, the atoms in the interstitial sites will push the host atoms apart so that the face-centered cubic lattice is somewhat opened up and loses its close-packing character.

The rock-salt structure

Alkali halides that crystallize with the "rock-salt" structure exemplified by sodium chloride can be regarded either as a FCC structure of one kind of ion in which the octahedral holes are occupied by ions of opposite charge, or as two interpenetrating FCC lattices made up of the two kinds of ions. The two shaded octahedra illustrate the identical coordination of the two kinds of ions; each atom or ion of a given kind is surrounded by six of the opposite kind, resulting in a coordination expressed as (6:6).

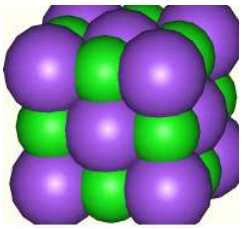


How many NaCl units are contained in the unit cell? If we ignore the atoms that were placed outside the cell in order to construct the octahedra, you should be able to count fourteen "orange" atoms and thirteen "blue" ones. But many of these are shared with adjacent unit cells.

An atom at the corner of the cube is shared by eight adjacent cubes, and thus makes a 1/8 contribution to any one cell. Similarly, the center of an edge is common to four other cells, and an atom centered in a face is shared with two cells. Taking all this into consideration, you should be able to confirm the following tally showing that there are four AB units in a unit cell of this kind.

Orange	**Blue**
8 at corners: 8 x 1/8 = 1	12 at edge centers: 12 x ¼ = 3
6 at face centers: 6 x ½ = 3	1 at body center = 1
total: 4	total: 4

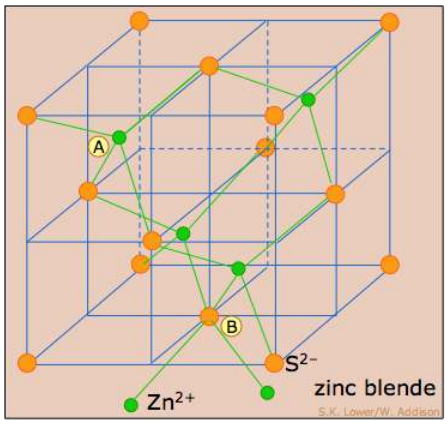
If we take into consideration the actual sizes of the ions (Na^+ = 116 pm, Cl^- = 167 pm), it is apparent that neither ion will fit into the octahedral holes with a CCP lattice composed of the other ion, so the actual structure of NaCl is somewhat expanded beyond the close-packed model.



The space-filling model on the right depicts a face-centered cubic unit cell of chloride ions (purple), with the sodium ions (green) occupying the octahedral sites.

The zinc-blende structure: using some tetrahedral holes

Since there are two tetrahedral sites for every atom in a close-packed lattice, we can have binary compounds of 1:1 or 1:2 stoichiometry depending on whether half or all of the tetrahedral holes are occupied. Zinc-blende is the mineralogical name for zinc sulfide, ZnS. An impure form known as *sphalerite* is the major ore from which zinc is obtained.

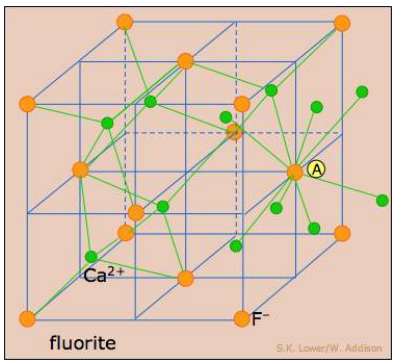


This structure consists essentially of a FCC (CCP) lattice of sulfur atoms (orange) (equivalent to the lattice of chloride ions in NaCl) in which zinc ions (green) occupy half of the tetrahedral sites. As with any FCC lattice, there are four atoms of sulfur per unit cell, and the the four zinc atoms are totally contained in the unit cell. Each atom in this structure has **four** nearest neighbors, and is thus tetrahedrally coordinated.

It is interesting to note that if all the atoms are replaced with carbon, this would correspond to the *diamond* structure.

The fluorite structure: all tetrahedral sites occupied

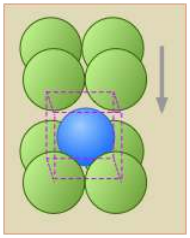
Fluorite, CaF_2, having twice as many ions of fluoride as of calcium, makes use of all eight tetrahedral holes in the CPP lattice of calcium ions (orange) depicted here. To help you understand this structure, we have shown some of the octahedral sites in the next cell on the right; you can see that the calcium ion at **A** is surrounded by eight fluoride ions, and this is of course the case for all of the calcium sites. Since each fluoride ion has four nearest-neighbor calcium ions, the coordination in this structure is described as (8:4).



Although the radii of the two ions (F^-= 117 pm, Ca^{2+} = 126 pm does not allow true close packing, they are similar enough that one could just as well describe the structure as a FCC lattice of fluoride ions with calcium ions in the octahedral holes.

Simple- and body-centered cubic structures

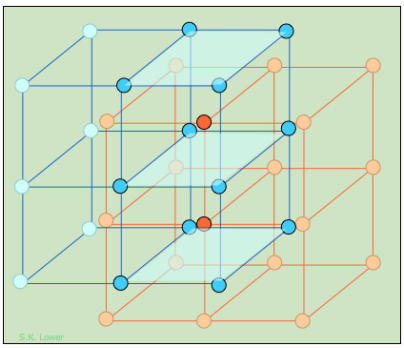
In Section 4 we saw that the only cubic lattice that can allow close packing is the face-centered cubic structure. The simplest of the three cubic lattice types, the *simple cubic lattice*, lacks the hexagonally-arranged layers that are required for close packing. But as shown in this exploded view, the void space between the two square-packed layers of this cell constitutes an octahedral hole that can accommodate another atom, yielding a packing arrangement that in favorable cases can approximate true close-packing. Each second-layer B atom (blue) resides within the unit cell defined the A layers above and below it.



The A and B atoms can be of the same kind or they can be different. If they are the same, we have a *body-centered cubic lattice*. If they are different, and especially if they are oppositely-charged ions (as in the CsCl structure), there are size restrictions: if the B atom is too large to fit into the interstitial space, or if it is so small that the A layers (which all carry the same electric charge) come into contact without sufficient A-B coulombic attractions, this structural arrangement may not be stable.

The cesium chloride structure

CsCl is the common model for the BCC structure. As with so many other structures involving two different atoms or ions, we can regard the same basic structure in different ways. Thus if we look beyond a single unit cell, we see that CsCl can be represented as two interpenetrating simple cubic lattices in which each atom occupies an octahedral hole within the cubes of the other lattice.



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13.5: Crystalline Solids- The Fundamental Types

Learning Objectives

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure 13.5.1).

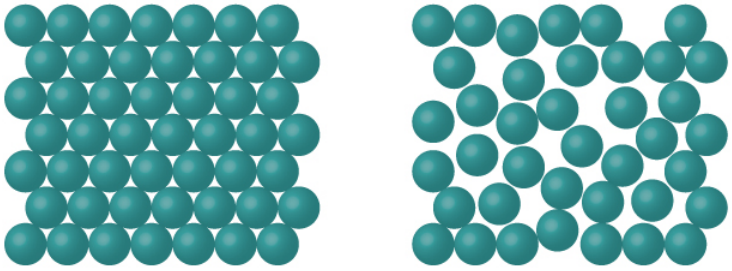


Figure 13.5.1: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

The crystalline arrangement shows many circles drawn in rows and stacked together tightly. The amorphous arrangement shows many circles spread slightly apart and in no organized pattern.

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as boron oxide (Figure 13.5.2), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

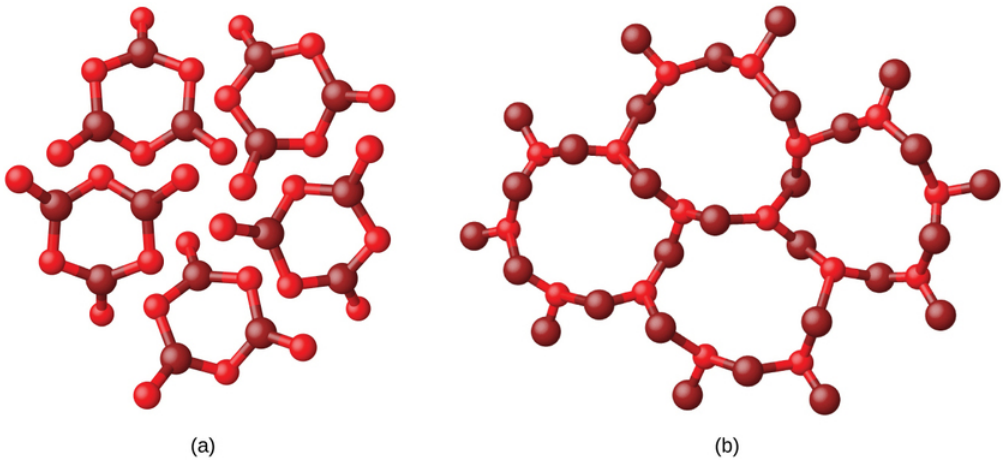


Figure 13.5.2: (a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

The first structure of diboron trioxide shows five identical and separated hexagonal rings. The second structure of diboron trioxide shows a more interconnected structure with four large rings forming a more stable structure.

Crystalline solids are generally classified according the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure 13.5.3). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

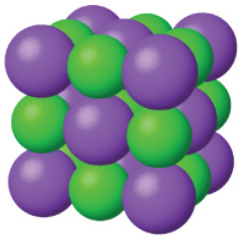


Figure 13.5.3: Sodium chloride is an ionic solid.

A cube composed of purple and green spheres is shown. The cube has dimensions of three by three spheres. The purple spheres are slightly larger than the green spheres.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 13.5.4. 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. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

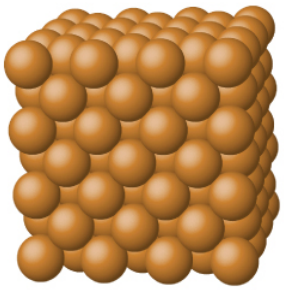


Figure 13.5.4: Copper is a metallic solid.

Covalent Network Solids

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure 13.5.5. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

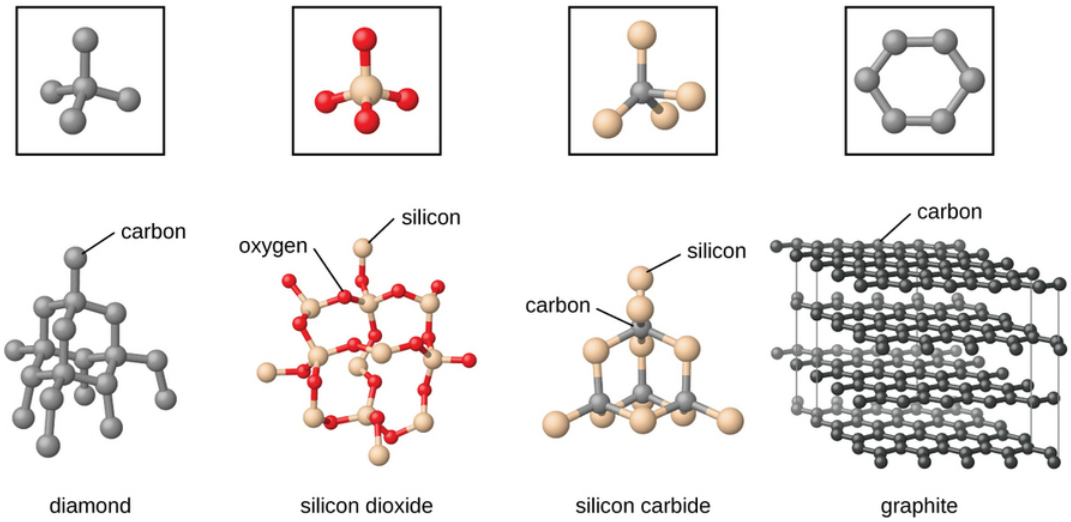


Figure 13.5.5. A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

The complex three dimensional structure of diamond, silicon dioxide, silicon carbide and graphite is shown along with a a smaller repeating unit of the structure shown above each structure.

Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure 13.5.6, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below −200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

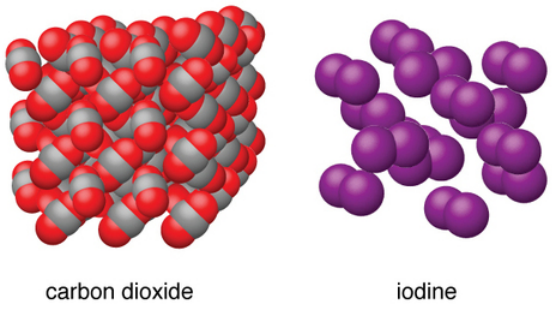


Figure 13.5.6: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

On the left, many red and grey molecules are densely stacked in a 3-D drawing to represent carbon dioxide. On the right, purple molecules are scattered randomly to represent iodine.

Properties of Solids

A crystalline solid, like those listed in Table 13.5.1 has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table 13.5.1: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure 13.5.7. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

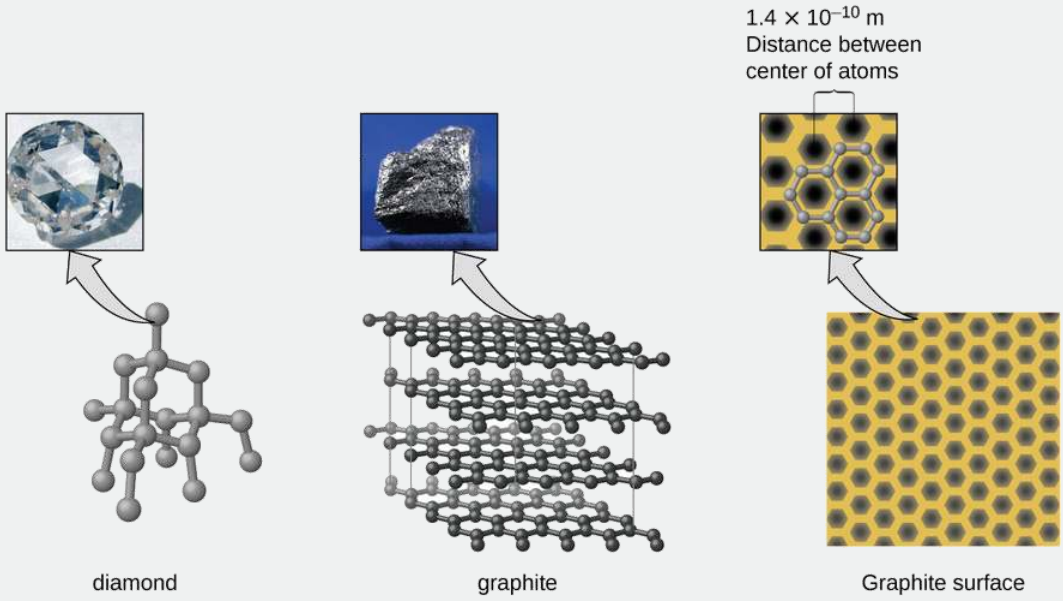


Figure 13.5.7: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

A close up of a piece of diamond shows a three dimensional sturcture of a complex network of well bonded carbon atoms. A close up of a graphite shows several layers of carbon sheets. Each sheet is composed of a repeated and connected hexagonal structure of carbon atoms. The third diagram shows that the distance between the center of atoms is 1.4 times 10 to the power of negative 10 meters.

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure 13.5.8, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

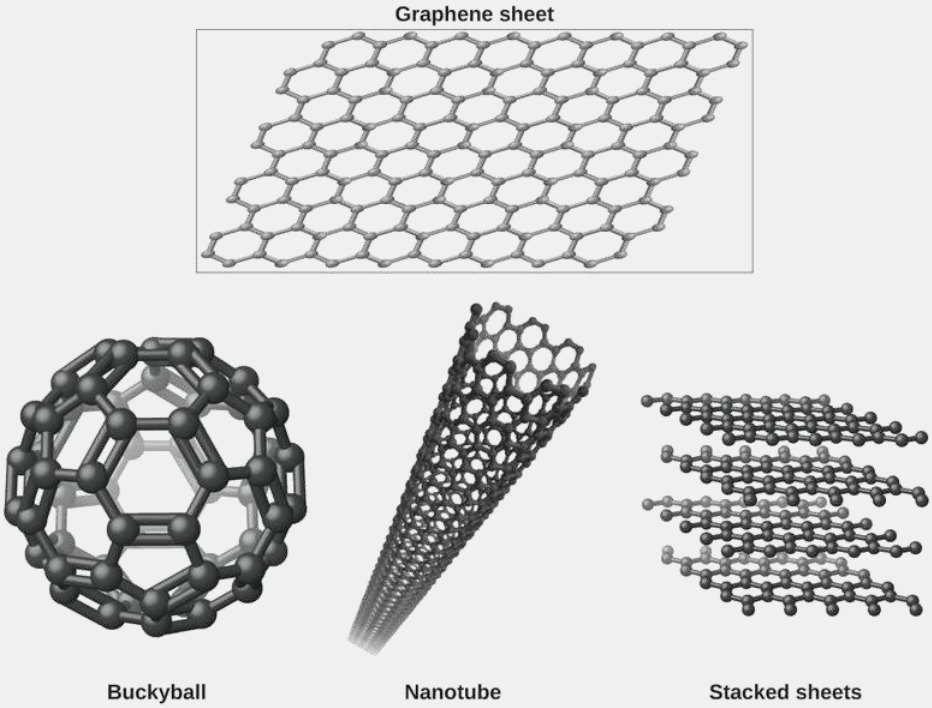


Figure 13.5.8: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

A sheet of interconnected hexagonal rings is shown at the top. Below it, a bukcyball is shown which is a sphere is composed of hexagonal rings. In the lower middle image, a nanotube is shown that is made by rolling a graphene sheet into a tube. In the lower right image, stacked sheets made up of four horizontal sheets composed of joined, hexagonal rings is shown.

Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure 13.5.9. Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.

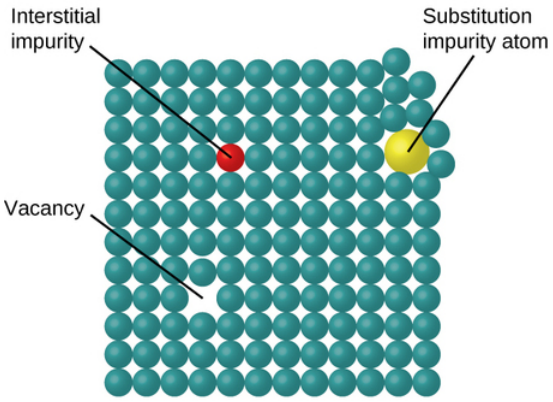


Figure 13.5.9: Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic

solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Glossary

amorphous solid
(also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid
solid whose particles are held together by covalent bonds

crystalline solid
solid in which the particles are arranged in a definite repeating pattern

interstitial sites
spaces between the regular particle positions in any array of atoms or ions

ionic solid
solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid
solid composed of metal atoms

molecular solid
solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy
defect that occurs when a position that should contain an atom or ion is vacant

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13.6: The Structure of Ionic Solids

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above.

- What is an ionic solid, what are its typical physical properties, and what kinds of elements does it contain?
- Define the lattice energy of an ionic solid in terms of the energetic properties of its component elements.
- Make a rough sketch that describes the structure of solid sodium chloride.
- Describe the role that the relative ionic radii play in contributing to the stability of an ionic solids.
- Give examples of some solids that can form when ionic solutions are evaporated, but which do not fall into the category of "ionic" solids.

In this section we deal mainly with a very small but important class of solids that are commonly regarded as composed of ions. We will see how the relative sizes of the ions determine the energetics of such compounds. And finally, we will point out that not all solids that are formally derived from ions can really be considered "ionic" at all.

Ionic Solids

The idealized ionic solid consists of two interpenetrating lattices of oppositely-charged point charges that are held in place by a balance of coulombic forces. But because real ions occupy space, no such "perfect" ionic solid exists in nature. Nevertheless, this model serves as a useful starting point for understanding the structure and properties of a small group of compounds between elements having large differences in electronegativity.

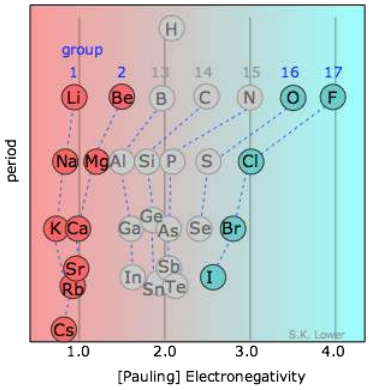


Figure 13.6.1

Chemists usually apply the term "ionic solid" to binary compounds of the metallic elements of Groups 1-2 with one of the halogen elements or oxygen. As can be seen from the diagram, the differences in electronegativity between the elements of Groups 1-2 and those of Group 17 (as well as oxygen in Group 16) are sufficiently great that the binding in these solids is usually dominated by Coulombic forces and the crystals can be regarded as built up by aggregation of oppositely-charged ions.

Sodium Chloride (rock-salt) Structure

The most well known ionic solid is sodium chloride, also known by its geological names as *rock-salt* or *halite*. We can look at this compound in both structural and energetic terms.



Rock Salt

Structurally, each ion in sodium chloride is surrounded and held in tension by six neighboring ions of opposite charge. The resulting crystal lattice is of a type known as *simple cubic*, meaning that the lattice points are equally spaced in all three dimensions and all cell angles are 90°.

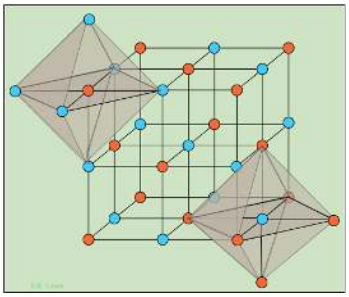


Figure 13.6.2: The differently-colored circles represent the Na^+ and Cl^- ions; because their locations are geometrically equivalent, it does not matter which color is assigned to which ion.

In Figure 13.6.2, we have drawn two imaginary octahedra centered on ions of different kinds and extending partially into regions outside of the diagram. (We could equally well have drawn them at any of the lattice points, but show only two in order to reduce clutter.) Our object in doing this is to show that each ion is surrounded by six other ions of opposite charge; this is known as *(6,6) coordination*. Another way of stating this is that each ion resides in an *octahedral hole* within the cubic lattice.

How can one sodium ion surrounded by six chloride ions (or *vice versa*) be consistent with the simplest formula NaCl? The answer is that each of those six chloride ions also sits at the center of its own octahedron defined by another six sodium ions. You might think that this corresponds to Na_6Cl_6, but note that the central sodium ion shown in the diagram can claim only a one-sixth share of each of its chloride ion neighbors, so the formula NaCl is not just the simplest formula, but correctly reflects the 1:1 stoichiometry of the compound. But of course, as in all ionic structures, there are no distinguishable "molecular" units that correspond to the NaCl simplest formula. Bear in mind that large amount of empty space in diagrams depicting a crystal lattice structure can be misleading, and that the ions are really in direct contact with each other to the extent that this is geometrically possible.

Sodium Chloride Energetics

Sodium chloride, like virtually all salts, is a more energetically favored configuration of sodium and chlorine than are these elements themselves; in other words, the reaction

$$Na_{(s)} + ½Cl_{2(g)} \rightarrow NaCl_{(s)} \tag{13.6.1}$$

is accompanied by a release of energy in the form of heat. How much heat, and why? To help us understand, we can imagine the formation of one mole of sodium chloride from its elements proceeding in these hypothetical steps in which we show the energies explicitly:

Step 1: *Atomization* of sodium (breaking one mole of metallic sodium into isolated sodium atoms)

$$\mathrm{Na\,(s)} + 108\,\mathrm{kJ} \longrightarrow \mathrm{Na\,(g)} \tag{13.6.2}$$

Step 2: Same thing with chlorine. This requires more energy because it involves breaking a covalent bond.

$$½\mathrm{Cl_2\,(g)} + 127\ \ k\,\mathrm{J} \longrightarrow \mathrm{Cl\,(g)} \tag{13.6.3}$$

Step 3: We strip an electron from one mole of sodium atoms (this costs a lot of energy!)

$$\mathrm{Na\,(g)} + 496\ \ k\,\mathrm{J} \longrightarrow \mathrm{Na^+\,(g)} + \mathrm{e^-} \tag{13.6.4}$$

Step 4: Feeding these electrons to the chlorine atoms gives most of this energy back.

$$\mathrm{Cl\,(g)} + \mathrm{e^-} \longrightarrow \mathrm{Cl^-\,(g)} + 348\ \ k\,\mathrm{J} \tag{13.6.5}$$

Step 5: Finally, we bring one mole of the ions together to make the crystal lattice — with a huge release of energy.

$$\mathrm{Na^+\,(g)} + \mathrm{Cl^-\,(g)} \longrightarrow \mathrm{NaCl\,(s)} + 787\ \ k\,\mathrm{J} \tag{13.6.6}$$

If we add all of these equations together, we get

$$\mathrm{Na\,(s)} + \tfrac{1}{2}\,\mathrm{Cl_2\,(g)} \longrightarrow \mathrm{NaCl\,(s)} + 404\ kJ \tag{13.6.7}$$

In other words, the formation of solid sodium chloride from its elements is highly *exothermic*. As this energy is released in the form of heat, it spreads out into the environment and will remain unavailable to push the reaction in reverse. We express this by saying that "sodium chloride is more *stable* than its elements".

Looking at the equations above, you can see that Equation 13.6.6 constitutes the big payoff in energy. The 787 kj/mol noted there is known as the NaCl *lattice energy*. Its large magnitude should be no surprise, given the strength of the coulombic force between ions of opposite charge.

It turns out that it is the lattice energy that renders the gift of stability to all ionic solids.Note that this lattice energy, while due principally to coulombic attraction between each ion and its eight nearest neighbors, is really the sum of *all* the interactions with the crystal. Lattice energies cannot be measured directly, but they can be estimated fairly well from the energies of the other processes described in the table immediately above.

How Geometry and Periodic Properties Interact

The most energetically stable arrangement of solids made up of identical molecular units (as in the noble gas elements and pure metals) are generally those in which there is a minimum of empty space; these are known as *close-packed* structures, and there are several kinds. In the case of ionic solids of even the simplest 1:1 stoichiometry, the positive and negative ions usually differ so much in size that packing is often much less efficient. This may cause the solid to assume lattice geometries that differ from the one illustrated above for sodium chloride.

By way of illustration, consider the structure of cesium chloride (the spelling *cæsium* is also used), CsCl. The radius of the Cs^+ ion is 168 pm compared to 98 pm for Na^+ and cannot possibly fit into the octahedral hole of a simple cubic lattice of chloride ions. The CsCl lattice therefore assumes a different arrangement.

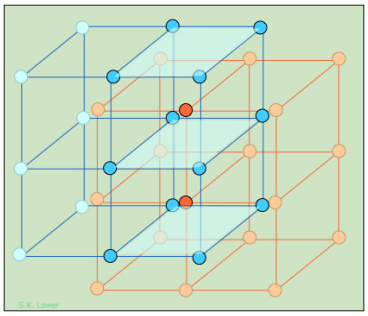


Figure 13.6.3: The CsCl structure, like that of NaCl, can be regarded as two interpenetrating lattices of the oppositely-charged ions. In CsCl, however, the metal ions, instead of being surrounded by six chloride ions, are shifted into the center of each cubic element of the Cl–-ion lattice.

Figure 13.6.3 focuses on two of these cubic lattice elements whose tops and bottoms are shaded for clarity. It should be easy to see that each cesium ion now has eight nearest-neighbor chloride ions. Each chloride ion is also surrounded by eight cesium ions, so all the lattice points are still geometrically equivalent. We therefore describe this structure as having *(8,8) coordination*.

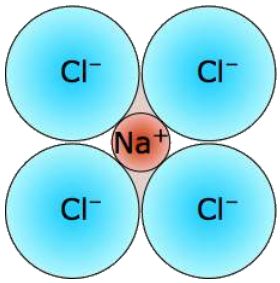
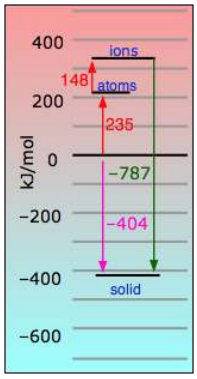
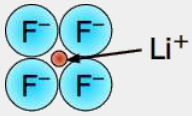
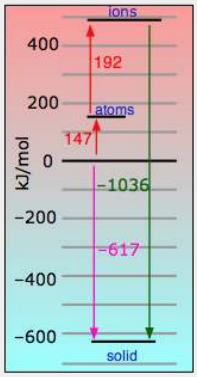
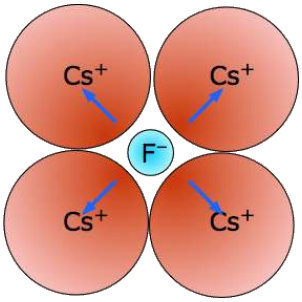
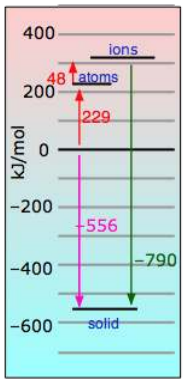
The two kinds of lattice arrangements exemplified by NaCl ("rock salt") and CsCl are found in a large number of other 1:1 ionic solids, and these names are used generically to describe the structures of these other compounds. There are of course many other

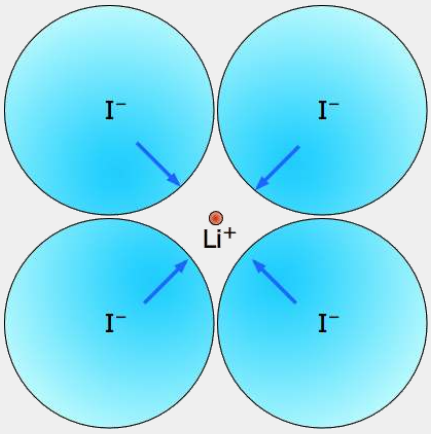
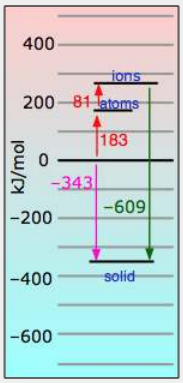
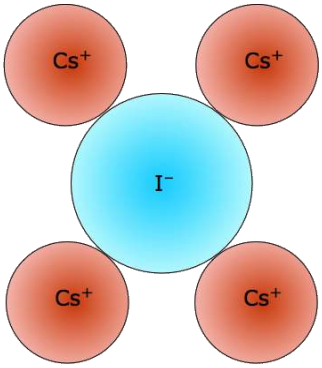
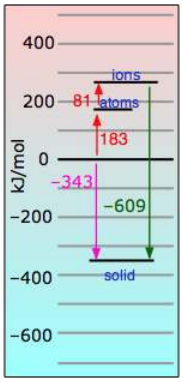
fundamental lattice arrangements (not all of them cubic), but the two we have described here are sufficient to illustrate the point that the *radius ratio* (the ratio of the radii of the positive to the negative ion) plays an important role in the structures of simple ionic solids.

The Alkali Halides

The interaction of the many atomic properties that influence ionic binding are nicely illustrated by looking at a series of alkali halides, especially those involving extreme differences in atomic radii. The latter are all drawn to the same scale. On the energetic

plots at the right, the lattice energies are shown in green. We will start with the one you already know very well.

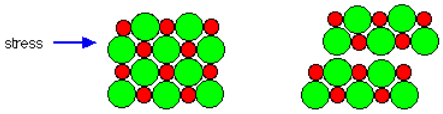
Sodium chloride - NaCl ("rock-salt") mp/bp 801/1413 °C; coordination (6,6)		
Lithium Fluoride - LiF - mp/bp 846/1676 °C, rock-salt lattice structure (6,6). Tiny-tiny makes strong-strong! This is the most "ionic" of the alkali halides, with the largest lattice energy and highest melting and boiling points. The small size of these ions (and consequent high charge densities) together with the large electronegativity difference between the two elements places a lot of electronic charge between the atoms. Even in this highly ionic solid, the electron that is "lost" by the lithium atom turns out to be closer to the Li nucleus than when it resides in the 2*s* shell of the neutral atom.		
Cesium Fluoride, CsF - mp/bp 703/1231 °C, (8,8) coordination. With five shells of electrons shielding its nucleus, the Cs^+ ion with its low charge density resembles a big puff-ball which can be distorted by the highly polarizing fluoride ion. The resulting ion-induced dipoles (blue arrows) account for much of the lattice energy here. The reverse of this would be a tiny metal ion trying to hold onto four relatively huge iodide ions like Lithium iodide.		

Lithium iodide, LiI - mp/bp 745/1410 °C. Negative ions can make even bigger puff-balls. The tiny lithium ion can't get very close to any of the iodides to generate a very strong coulombic binding, but does polarize them to create an ion-induced dipole component. It does not help that the negative ions are in contact with each other. The structural geometry is the same (6,6) coordination as NaCl.		
Cesium iodide, CsI - mp/bp 626/1280 °C. Even with the (8,8) coordination afforded by the CsCl structure, this is a pretty sorry combination owing to the low charge densities. The weakness of coulombic- compared to van der Waals interactions makes this the least-"ionic" of all the alkali halide solids.		

Conclusion: Many of the alkali halide solids are not all that "ionic" in the sense that coulombic forces are the predominant actors; in many, such as the CsI illustrated above, ion-induced dipole forces are more important.

Some Properties of Ionic Solids

As noted above, ionic solids are generally hard and brittle. Both of these properties reflect the strength of the coulombic force. *Hardness* measures resistance to *deformation*. Because the ions are tightly bound to their oppositely-charged neighbors and, a mechanical force exerted on one part of the solid is resisted by the electrostatic forces operating over an extended volume of the crystal.



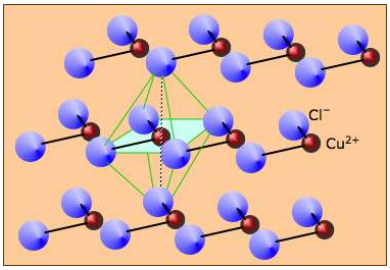
But by applying sufficient force, one layer of ions can be made to slip over another; this is the origin of *brittleness*. This slippage quickly propagates along a plane of the crystal (more readily in some directions than in others), weakening their attraction and leading to physical *cleavage*. Because the "ions" in ionic solids lack *mobility*, the solids themselves are **electrical insulators**.

Not all ion-derived solids are "ionic".

Even within the alkali halides, the role of coulombic attraction diminishes as the ions become larger and more polarizable or differ greatly in radii. This is especially true of the anions, which tend to be larger and whose electron clouds are more easily distorted. In solids composed of polyatomic ions such as $(NH_4)_2SO_4$, $SrClO_4$, NH_4CO_3, ion-dipole and ion-induced dipole forces may actually be stronger than the coulombic force. Higher ionic charges help, especially if the ions are relatively small. This is especially evident in the extremely high melting points of the Group 2 and higher oxides:

MgO (magnesia)	CaO (lime)	SrO (strontia)	Al2O3 (alumina)	ZrO2 (zirconia)
2830 °C	2610 °C	2430 °C	2050 °C	2715 °C

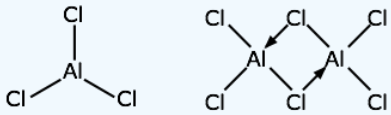
These substances are known as *refractories*, meaning that they retain their essential properties at high temperatures. Magnesia, for example, is used to insulate electric heating elements and, in the form of fire bricks, to line high-temperature furnaces. No boiling points have been observed for these compounds; on further heating, they simply dissociate into their elements. Their crystal structures can be very complex, and some (notably Al_2O_3) can have several solid forms. Even in the most highly ionic solids there is some electron sharing, so the idea of a “pure” ionic bond is an abstraction.



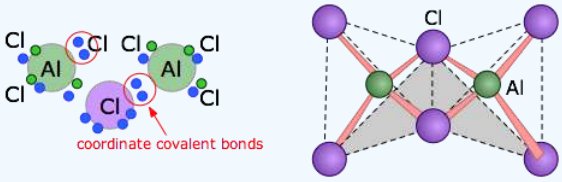
Many solids that are formally derived from ions cannot really be said to form "ionic" solids at all. For example, anhydrous copper(II) chloride consists of layers of copper atoms surrounded by four chlorine atoms in a square arrangement. Neighboring chains are offset so as to create an octahedral coordination of each copper atom. Similar structures are commonly encountered for other salts of transition metals. Similarly, most oxides and sulfides of metals beyond Group 2 tend to have structures dominated by other than ion-ion attractions.

Aluminum Halides

The trihalides of aluminum offer another example of the dangers of assuming ionic character of solids that are formally derived from ions. Aqueous solutions of what we assume to be AlF_3, $AlCl_3$, $AlBr_3$, and AlI_3 all exhibit the normal properties ionic solutions (they are electrically conductive, for example), but the solids are quite different: the melting point of AlF_3 is 1290°C, suggesting that it is indeed ionic. But $AlCl_3$ melts at 192°C — hardly consistent with ionic bonding, and the other two halides are also rather low-melting. Structural studies show that when $AlCl_3$ vaporizes or dissolves in a non-polar solvent it forms a dimer Al_2Cl_6. The two other halides exist only as dimers in all states.



The structural formula of the Al_2Cl_6 molecule shows that the aluminum atoms are bonded to four chlorines, two of which are shared between the two metal atoms. The arrows represent coordinate covalent bonds in which the bonding electrons both come from the same atom (chlorine in this case.)



As shown at the right above, the aluminum atoms can be considered to be located at the centers of two tetrahedra that possess one edge in common.

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13.7: Network Covalent Atomic Solids- Carbon and Silicates

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 13.7.1, 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.

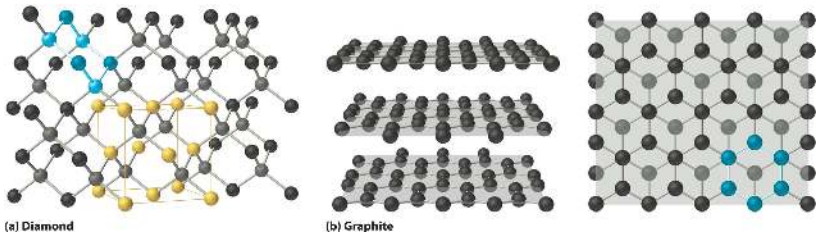


Figure 13.7.1: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure 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.

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 13.7.1. 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 13.7.2 compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 13.7.2: A Comparison of Intermolecular (ΔHsub) 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.

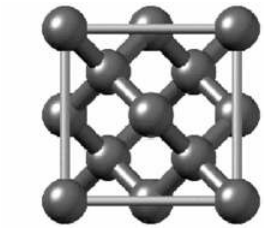


Figure 13.7.2: Rotating model of diamond cubic. Figure used with permission from Wikipedia

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 13.7.3 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.

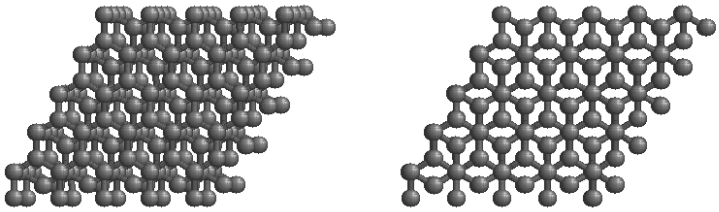


Figure 13.7.3: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

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 theoretians 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.

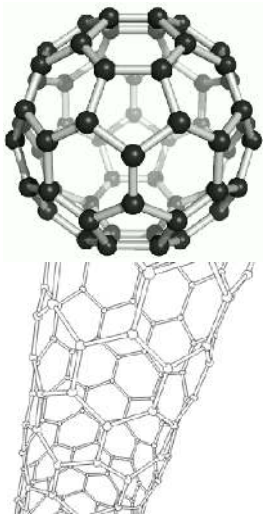


Figure 13.7.4: Example of fullerenes: a buckyball (C_{60} *on left and an extended bucktube. Images used with permission from Wikipedia.*

The C_{60} molecule (Figure 13.7.4; 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 13.7.4; right). All of these substances are pure carbon.

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?

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CHAPTER OVERVIEW

14: Solutions

14.2: Types of Solutions and Solubility

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14.2: Types of Solutions and Solubility

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 14.2.1 lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table 14.2.1: Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)
solid	solid	solid	alloys and other "solid solutions"

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$\mathrm{Zn(NO_3)_2\,(s) + H_2O\,(l)\ \rightarrow Zn^{2+}\,(aq) + 2\,NO_3^-\,(aq)} \tag{14.2.1}$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq)\ \rightarrow Zn^{2+}\,(aq) + 2\,Cl^-\,(aq) + H_2\,(g)} \tag{14.2.2}$$

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation (that it is a physical change).

> *Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.*

Substances that form a single homogeneous phase in all proportions are said to be completely *miscible* in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and

water, they are *immiscible*. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation (or hydration when the solvent is water). Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH_1, ΔH_2, and ΔH_3 in Figure 14.2.2. The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{14.2.3}$$

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (−3791 kJ/mol), are generally insoluble in all solvents.

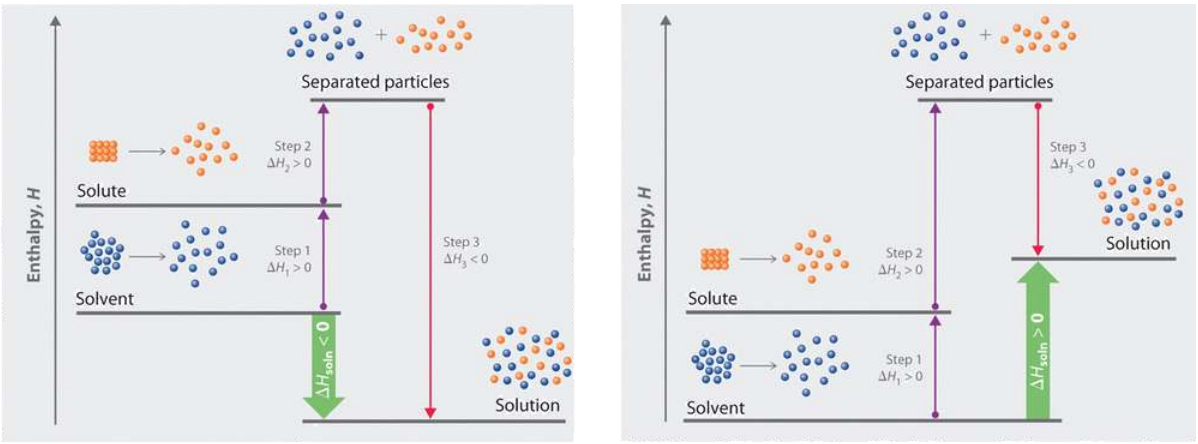


Figure 14.2.2: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 14.2.3).



Figure 14.2.3: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Entropy and Solution Formation

The enthalpy change that accompanies a process is important because processes that release substantial amounts of energy tend to occur spontaneously. A second property of any system, its entropy, is also important in helping us determine whether a given process occurs spontaneously. We will discuss entropy in more detail elsewhere, but for now we can state that entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. A perfect crystal at 0 K, whose atoms are regularly arranged in a perfect lattice and are motionless, has an entropy of zero. In contrast, gases have large positive entropies because their molecules are highly disordered and in constant motion at high speeds.

The formation of a solution disperses molecules, atoms, or ions of one kind throughout a second substance, which generally increases the disorder and results in an increase in the entropy of the system. Thus entropic factors almost always favor formation of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and n-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔH_{soln} should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the n-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative ΔH_{soln} but rather the increase in entropy due to the increased disorder in the mixture. All spontaneous processes with $\Delta H \geq 0$ are characterized by an *increase* in entropy. In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

> *All spontaneous processes with $\Delta H \geq 0$ are characterized by an increase in entropy.*

Table 14.2.2 summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

Table 14.2.2: Relative Changes in Enthalpies for Different Solute–Solvent Combinations*

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} ($\Delta H_1 + \Delta H_2 + \Delta H_3$)	Result of Mixing Solute and Solvent†
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form
small; positive	small; positive	small; negative	small; positive or negative	solution will usually form

*ΔH_1, ΔH_2, and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in Figure 14.2.2.
†In all four cases, entropy increases.

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 14.2.4). Consequently, all gases dissolve readily in one another in all proportions to form solutions.

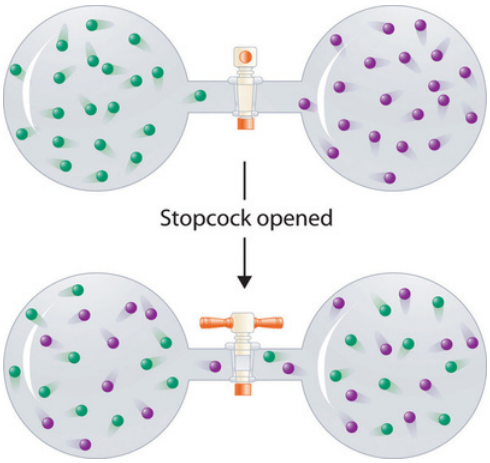
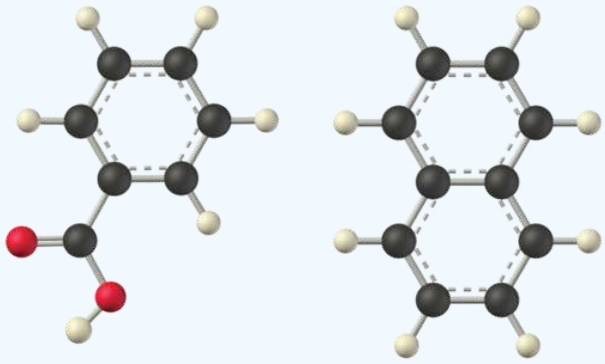


Figure 14.2.4: Formation of a Solution of Two Gases. (top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

Example 14.2.1

Considering LiCl, benzoic acid ($C_6H_5CO_2H$), and naphthalene, which will be most soluble and which will be least soluble in water?



Given: three compounds

Asked for: relative solubilities in water

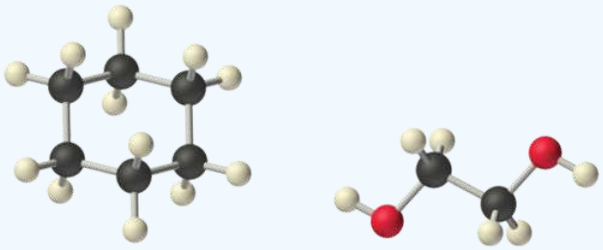
Strategy: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 14.2.2. Then use Table 14.2.2 to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in Equation 14.2.1). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.

? Exercise 14.2.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?



Answer

The most soluble is cyclohexane; the least soluble is ammonium chloride.

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible. Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration. The overall enthalpy change that accompanies the formation of a solution, ΔH_{soln}, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{soln} < 0$) processes favor solution formation. In addition, the change in entropy, the degree of disorder of the system, must be considered when predicting whether a solution will form. An increase in entropy (a decrease in order) favors dissolution.

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14.3: Energetics of Solution Formation

Learning Objectives

- Understand entropy drives solution formation but necessary enthalpy changes can prevent solution formation.
- Define heat of solute and heat of solvent, know these are always endothermic. (*"the price you pay to pull substances apart"*)
- Define heat of mixing, know this is always exothermic. (*"energy that splashes out when you drop atoms into each others energy well"*)
- Define heat of solvation, identify when it will be exothermic and when it will be endothermic.
- Define heat of hydration, know this is the sum of heat of mixing and heat of solvent when the solvent is water.
- Relate lattice energy to heat of solute.
- Given a substances lattice energy and heat of hydration, determine heat of solvation for that substance in water.
- Use the magnitude of changes in enthalpy to predict whether a given solute–solvent combination can 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 14.3.1 lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

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 14.3.2. The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{14.3.1}$$

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.

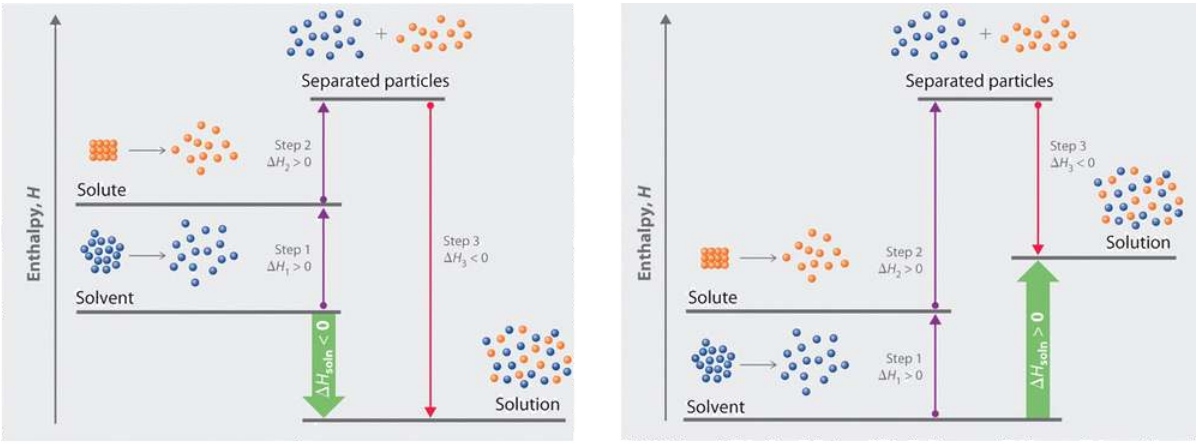


Figure 14.3.2: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 14.3.3).



Figure 14.3.3: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

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of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and n-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔH_{soln} should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the n-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative ΔH_{soln} but rather the increase in entropy due to the increased disorder in the mixture. All spontaneous processes with $\Delta H \geq 0$ are characterized by an *increase* in entropy. In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

> *All spontaneous processes with ΔH ≥ 0 are characterized by an increase in entropy.*

Table 14.3.2 summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

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ΔH_1 **(separation of solvent molecules)**	ΔH_2 **(separation of solute particles)**	ΔH_3 **(solute–solvent interactions)**	ΔH_{soln} **(**$\Delta H_1 + \Delta H_2 + \Delta H_3$**)**	**Result of Mixing Solute and Solvent†**
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form
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*ΔH_1, ΔH_2, and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in Figure 14.3.2.
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In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 14.3.4). Consequently, all gases dissolve readily in one another in all proportions to form solutions.

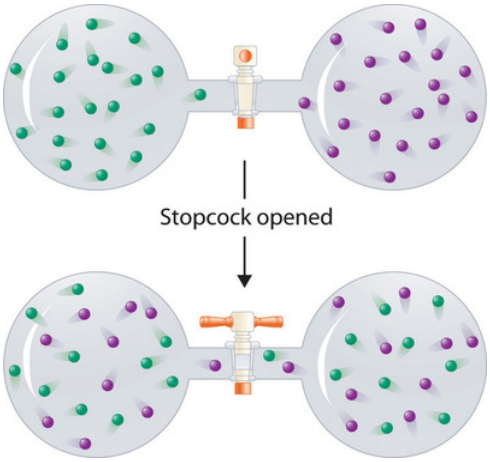
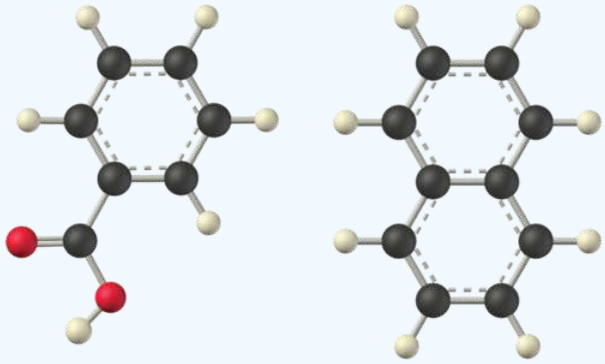


Figure 14.3.4: Formation of a Solution of Two Gases. (top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

Example 14.3.1

Considering LiCl, benzoic acid ($\mathrm{C_6H_5CO_2H}$), and naphthalene, which will be most soluble and which will be least soluble in water?



Benzoic acid Naphthalene

Given: three compounds

Asked for: relative solubilities in water

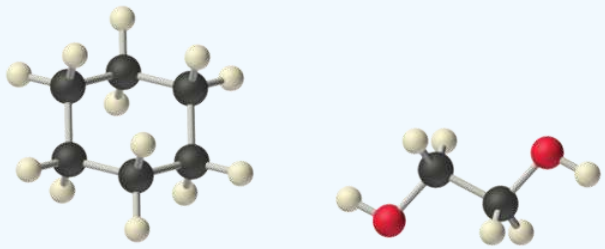
Strategy: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 14.3.2. Then use Table 14.3.2 to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in Equation ???). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.

Exercise 14.3.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?



Cyclohexane Ethylene glycol

Answer

> The most soluble is cyclohexane; the least soluble is ammonium chloride.

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible. Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration. The overall enthalpy change that accompanies the formation of a solution, ΔH_{soln}, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{soln} < 0$) processes favor solution formation. In addition, the change in entropy, the degree of disorder of the system, must be considered when predicting whether a solution will form. An increase in entropy (a decrease in order) favors dissolution.

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14.4: Solution Equilibrium and Factors Affecting Solubility

Learning Objectives

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

Effect of Temperature on the Solubility of Solids

Figure 14.4.1 shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and 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.

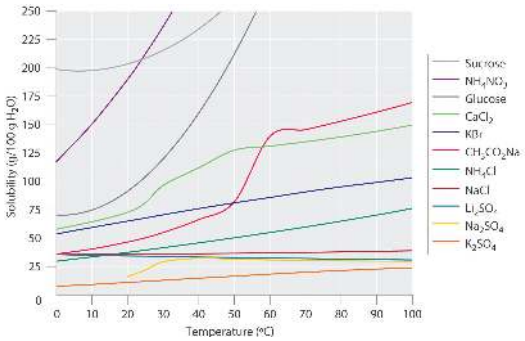


Figure 14.4.1: Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-SA-NC; anonymous)

Graph of solubility against temperature. Plots of sucrose, NH4NO3, glucose, CaCl2, KBr, CH3CO2Na, NH4Cl, Li2SO4, Na2SO4, K2SO4.

Notice in particular the curves for 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 14.4.1 shows that the solubility of both compounds increases sharply with increasing temperature. In fact, the magnitudes of the changes in both enthalpy and entropy for dissolution are temperature dependent. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate (CH_3CO_2Na) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C. According to the temperature curves in Figure 14.4.1, both compounds dissolve in water at 80°C, and all 50 g of KBr remains in solution at 0°C. Only about 36 g of CH_3CO_2Na are soluble in 100 g of water at 0°C, however, so approximately 114 g (150 g − 36 g) of CH_3CO_2Na crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original CH_3CO_2Na in essentially pure form in only one step.

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 14.4.1 and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be more soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

Effect of Temperature on the Solubility of Gases

The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 14.4.2. Attractive intermolecular interactions in the gas phase are essentially zero for most substances. When a gas dissolves, it does so because its molecules interact with solvent molecules. Because heat is released when these new attractive interactions form, dissolving most gases in liquids is an exothermic process ($\Delta H_{soln} < 0$). Conversely, adding heat to the solution provides thermal energy that overcomes the attractive forces between the gas and the solvent molecules, thereby decreasing the solubility of the gas. The phenomenon is similar to that involved in the increase in the vapor pressure of a pure liquid with increasing temperature. In the case of vapor pressure, however, it is attractive forces between solvent molecules that are being overcome by the added thermal energy when the temperature is increased.

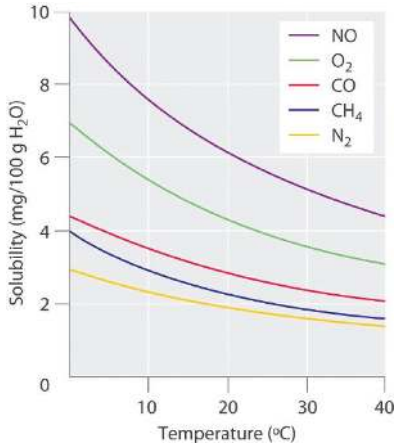


Figure 14.4.2: Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm. The solubilities of all gases decrease with increasing temperature. (CC BY-SA-NC; anonymous)

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called "boiler scale," a deposit that can seriously decrease the capacity of hot water pipes (Figure 14.4.3). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex and will be described elsewhere, but the driving force is the loss of dissolved CO_2 from solution. Hard water contains dissolved Ca^{2+} and HCO_3^- (bicarbonate) ions. Calcium bicarbonate ($Ca(HCO_3)_2$ is rather soluble in water, but calcium carbonate ($CaCO_3$) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

$$2\,HCO_3^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l) + CO_2(aq) \tag{14.4.1}$$

Heating the solution decreases the solubility of CO_2, which escapes into the gas phase above the solution. In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.



Figure 14.4.3: Calcium carbonate deposits (left) Calcium carbonate ($CaCO_3$) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved CO_2 is driven into the gas phase at high temperatures. (right) Highly calcified remains of Eiffel aqueduct near Euskirchen-Kreuzweingarten, Germany. (Wikipedia)

Thermal Pollution

In **thermal pollution**, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of O_2 at higher temperatures (Figure 14.4.2), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water.



There are many causes of fish kill, but oxygen depletion is the most common cause. (Public Domain; United States Fish and Wildlife Service)

A similar effect is seen in the rising temperatures of bodies of water such as the k0oi89Chesapeake Bay, the largest estuary in North America, where \lobal warming has been implicated as the cause. For each 1.5°C that the bay's water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter feeders, which then decreased light transmission to allow the eelsgrass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 14.4.4, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

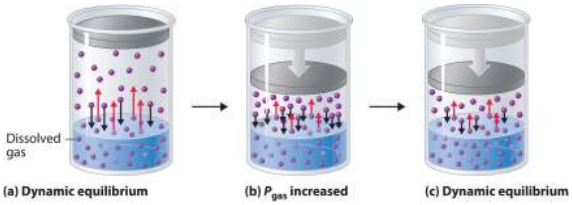


Figure 14.4.4: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established. (CC BY-SA-NC; anonymous)

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = kP \tag{14.4.2}$$

where

- C is the concentration of dissolved gas at equilibrium,
- P is the partial pressure of the gas, and
- k is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 14.4.1.

As the data in Table 14.4.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the Group 18 elements, the Henry's law constants increase smoothly from He to Ne to Ar.

Table 14.4.1: Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
He	3.9
Ne	4.7
Ar	15
H_2	8.1
N_2	7.1
O_2	14
CO_2	392

Oxygen is Especially Soluble

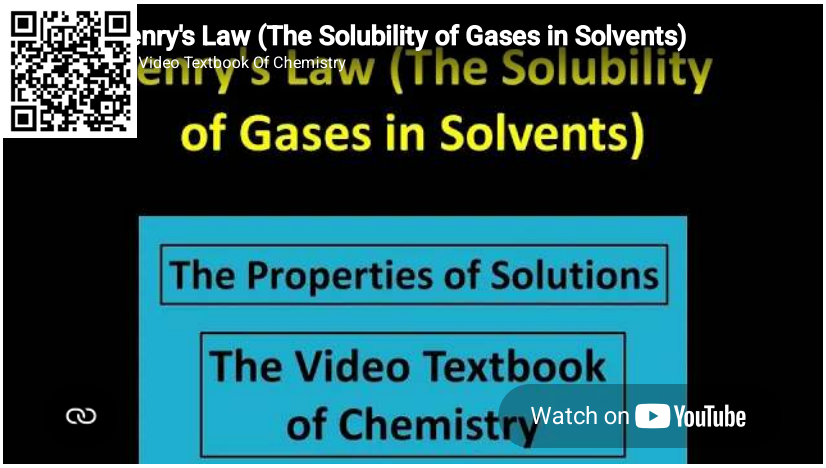
Nitrogen and oxygen are the two most prominent gases in the Earth's atmosphere and they share many similar physical properties. However, as Table 14.4.1 shows, O_2 is twice as soluble in water as N_2. Many factors contribute to solubility including the nature of the intermolecular forces at play. For a details discussion, see "The O_2/N_2 Ratio Gas Solubility Mystery" by Rubin Battino and Paul G. Seybold (J. Chem. Eng. Data 2011, 56, 5036–5044),

Gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S, and NH_3, do **not** obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $H^+(aq)$ and $Cl^-(aq)$, not dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

> *Gases that react with water do not obey Henry's law.*

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.



A Video Discussing Henry's Law. Video Link: Henry's Law (The Solubility of Gases in Solvents), YouTube(opens in new window) [youtu.be]

Example 14.4.1

The Henry's law constant for O_2 in water at 25°C is $1.27 \times 10^{-3} M/atm$, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at 25°C at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of O_2, and pressure

Asked for: solubility

Strategy:

A. Use Dalton's law of partial pressures to calculate the partial pressure of oxygen. (For more information about Dalton's law of partial pressures)
B. Use Henry's law to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2:

$$\begin{aligned} P_A &= \chi_A P_t \\ &= (0.21)(1.00\ atm) \\ &= 0.21\ atm \end{aligned}$$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$\begin{aligned} [\mathrm{CO_2}] &= kP_{\mathrm{O_2}} \\ &= (1.27 \times 10^{-3}\ M/\cancel{atm})(0.21\ \cancel{atm}) \\ &= 2.7 \times 10^{-4}\ M \end{aligned}$$

Exercise 14.4.1

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved $\mathrm{CO_2}$ in a soft drink:

a. bottled under a pressure of 5.0 atm of $\mathrm{CO_2}$
b. in equilibrium with the normal partial pressure of $\mathrm{CO_2}$ in the atmosphere (approximately $3 \times 10^{-4}\ atm$). The Henry's law constant for $\mathrm{CO_2}$ in water at 25°C is $3.4 \times 10^{-2}\ M/atm$.

Answer a

$0.17M$

Answer b

$1 \times 10^{-5}M$

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry's law describes the relationship between the pressure and the solubility of a gas.

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14.5: Expressing 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 14.5.1 reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 14.5.1: 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.

$$\text{moles } CH_3CO_2H = \frac{3.78 \cancel{\text{ g}}\ CH_3CO_2H}{60.05 \cancel{\text{ g}}/\text{mol}}$$

$$= 0.0629 \text{ mol}$$

The volume of the solution equals its mass divided by its density.

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

$$= \frac{100.0 \cancel{\text{ g}}\ \text{solution}}{1.00 \cancel{\text{ g}}/\text{mL}} = 100\ mL$$

Then calculate the molarity directly.

$$\text{molarity of } CH_3CO_2H = \frac{\text{moles } CH_3CO_2H}{\text{liter solution}}$$

$$= \frac{0.0629\ mol\ CH_3CO_2H}{(100 \cancel{\text{ mL}})(1\ L/1000 \cancel{\text{ mL}})} = 0.629\ M\ CH_3CO_2H$$

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:

$$\begin{aligned}\chi_{CH_3CO_2H} &= \frac{moles\ CH_3CO_2H}{moles\ CH_3CO_2H + moles\ H_2O} \\ &= \frac{0.0629\ mol}{0.0629\ mol + 5.34\ mol} \\ &= 0.0116 = 1.16 \times 10^{-2}\end{aligned}$$

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 14.5.1: 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

6.10 M HCl

Answer b

χ_{HCl}= 0.111

The concentration of a solution can also be described by its molality (m), the number of moles of solute per kilogram of solvent:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{14.5.1}$$

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):

$$\text{mass percentage} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{14.5.2}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{14.5.3}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{14.5.4}$$

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 14.5.2: 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 14.5.2: 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

4.3×10^{-8} M

Answer b

2×10^{-6} g

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 14.5.1 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 14.5.3.

Table 14.5.1: 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 14.5.3: 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 14.5.3: 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

mass percentage toluene = 24.8%

Answer b

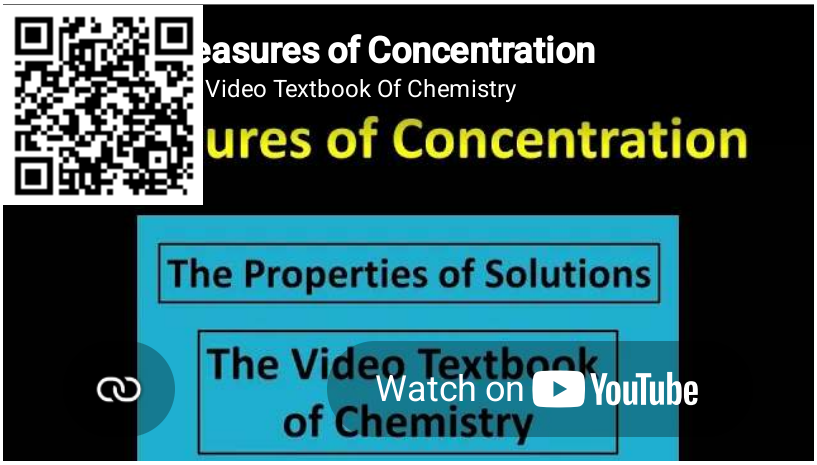
$\chi_{toluene}$= 0.219

Answer c

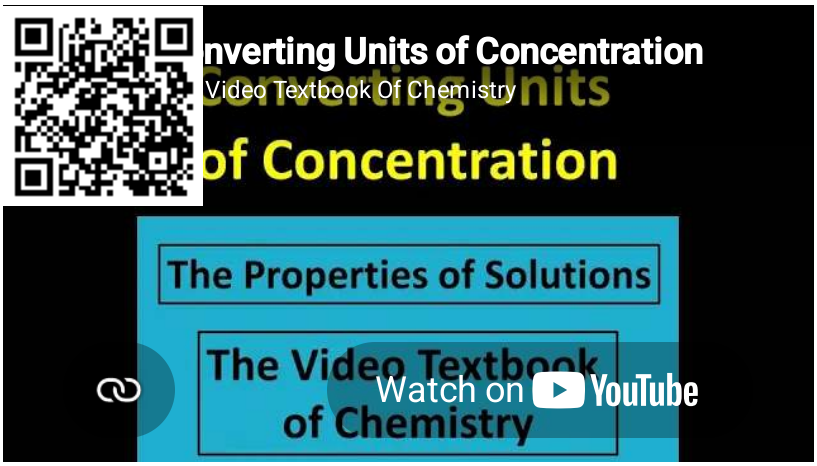
2.35 M toluene

Answer d

3.59 m toluene



A Video Discussing Different Measures of Concentration. Video Link: Measures of Concentration, YouTube (opens in new window) [youtu.be]



A Video Discussing how to Convert Measures of Concentration. Video Link: Converting Units of Concentration, YouTube(opens in new window) [youtu.be]

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.

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14.6: Colligative Properties- Freezing Point Depression, Boiling Point Elevation, and Osmosis

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol (“antifreeze”) to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin colligatus, meaning “bound together” as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

Counting concentrations

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, NaCl, and $\mathrm{CaCl_2}$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both NaCl and $\mathrm{CaCl_2}$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of NaCl contains 0.01 M $\mathrm{Na^+}$ ions and 0.01 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M $\mathrm{Ca^{2+}}$ ions and 0.02 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.03 M. These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete.

At **higher concentrations** (typically >1 M), especially with salts of small, highly charged ions (such as $\mathrm{Mg^{2+}}$ or $\mathrm{Al^{3+}}$), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind.

Vapor Pressure of Solutions and Raoult’s Law

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure 14.6.1, 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.

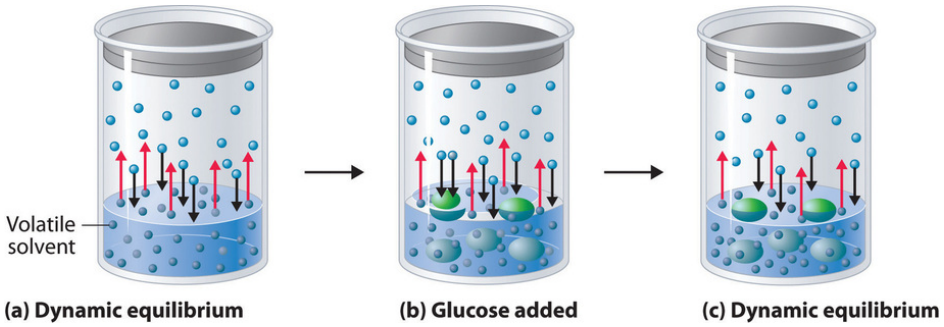


Figure 14.6.1: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile 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 14.6.2 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.

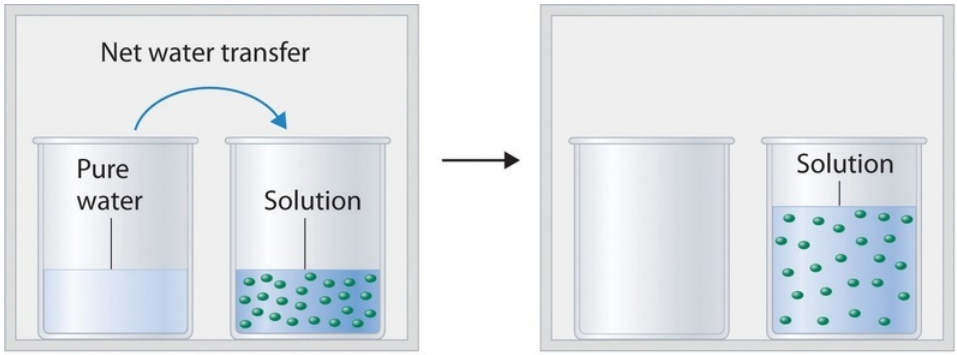


Figure 14.6.2: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water 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

$$P_A = \chi_A P_A^0 \tag{14.6.1}$$

where P_A is the vapor pressure of component A of the solution (in this case the solvent), χ_A is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 14.6.1 is known as **Raoult's law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then $\chi_A + \chi_B = 1$, and we can substitute $\chi_A = 1 - \chi_B$ to obtain

$$P_A = (1 - \chi_B)P_A^0 \tag{14.6.2}$$

$$= P_A^0 - \chi_B P_A^0 \tag{14.6.3}$$

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:

$$P_A^0 - P_A = \Delta P_A \tag{14.6.4}$$

$$= \chi_B P_A^0 \tag{14.6.5}$$

We can solve vapor pressure problems in either of two ways: by using Equation 14.6.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 14.6.5 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

Example 14.6.1: Anti-Freeze

Ethylene glycol ($HOCH_2CH_2OH$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

Given: identity of solute, percentage by mass, and vapor pressure of pure solvent

Asked for: vapor pressure of solution

Strategy:

A. Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.
B. Use Raoult's law to calculate the vapor pressure of the solution.

Solution:

A A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ \cancel{g})\left(\frac{1\ mol}{62.07\ \cancel{g}}\right) = 4.87\ mol\ EG$$

$$moles\ H_2O = (698\ \cancel{g})\left(\frac{1\ mol}{18.02\ \cancel{g}}\right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$\chi_{H_2O} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

B From Raoult's law (Equation 14.6.1), the vapor pressure of the solution is

$$P_{H_2O} = (\chi_{H2_O})(P^0_{H_2O})$$
$$= (0.888)(760\ mmHg) = 675\ mmHg$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 14.6.5 to calculate the resulting decrease in vapor pressure:

$$\chi_{EG} = \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O} = 0.112$$

$$\Delta P_{H2_O} = (\chi_{EG})(P^0_{H_2O}) = (0.112)(760\ mmHg) = 85.1\ mmHg$$

$$P_{H_2O} = P^0_{H_2O} - \Delta P_{H_2O} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

? Exercise 14.6.1

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

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.

Even when a solute is volatile, meaning that it has a measurable vapor pressure, we can still use Raoult's law. In this case, we calculate the vapor pressure of each component separately. The total vapor pressure of the solution (P_{tot}) is the sum of the vapor pressures of the components:

$$P_{tot} = P_A + P_B = \chi_A P_A^0 + \chi_B P_B^0 \tag{14.6.6}$$

Because $\chi_B = 1 - \chi_A$ for a two-component system,

$$P_{tot} = \chi_A P_A^0 + (1 - \chi_A) P_B^0 \tag{14.6.7}$$

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

$$P_{C_6H_6} = \chi_{C_6H_6} P^0_{C_6H_6} \tag{14.6.8}$$

and the vapor pressure of toluene in the solution is

$$PC_6H_5CH_3 = \chi_{C_6H_5CH_3} P^0_{C_6H_5CH3} \tag{14.6.9}$$

Equations 14.6.8 and 14.6.9 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 14.6.3. 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.

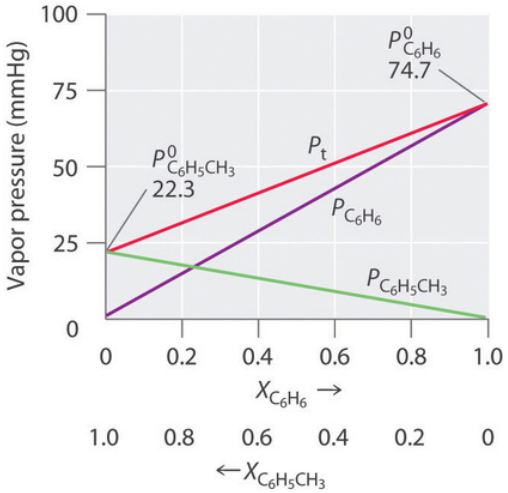


Figure 14.6.3: Vapor Pressures of Benzene–Toluene Solutions. Plots of the vapor pressures of benzene (C_6H_6) and toluene ($C_6H_5CH_3$) versus the mole fractions at 20°C are straight lines. For a solution like this, which approximates an ideal solution, the total vapor pressure of the solution (P_{tot}) is the sum of the vapor pressures of the components.

Graph of vapp pressure in mmHg against benzene and toulen mole fractions. Benzene mole fractions increase from left to right while toluene mole fractions decrease from left to right on the x axis.

A solution of two volatile components that behaves like the solution in Figure 14.6.3, 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 14.6.2

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 (Equation 14.6.1)

Strategy:

Identify whether each liquid is polar or nonpolar, and then predict the type of intermolecular interactions that occur in solution.

Solution:

a. Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is nonpolar. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. Hence the A–B interactions will be weaker than the A–A and B–B interactions, leading to a higher vapor pressure than predicted by Raoult's law (a positive deviation).
b. Methanol contains an extensive hydrogen bonding network, but in this case the polar acetone molecules create A–B interactions that are stronger than the A–A or B–B interactions, leading to a negative enthalpy of solution and a lower vapor pressure than predicted by Raoult's law (a negative deviation).
c. Hexane and isooctane are both nonpolar molecules (isooctane actually has a very small dipole moment, but it is so small that it can be ignored). Hence the predominant intermolecular forces in both liquids are London dispersion forces. We expect the A–B interactions to be comparable in strength to the A–A and B–B interactions, leading to a vapor pressure in good agreement with that predicted by Raoult's law (an ideal solution).

Exercise 14.6.2

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

approximately equal

Answer b

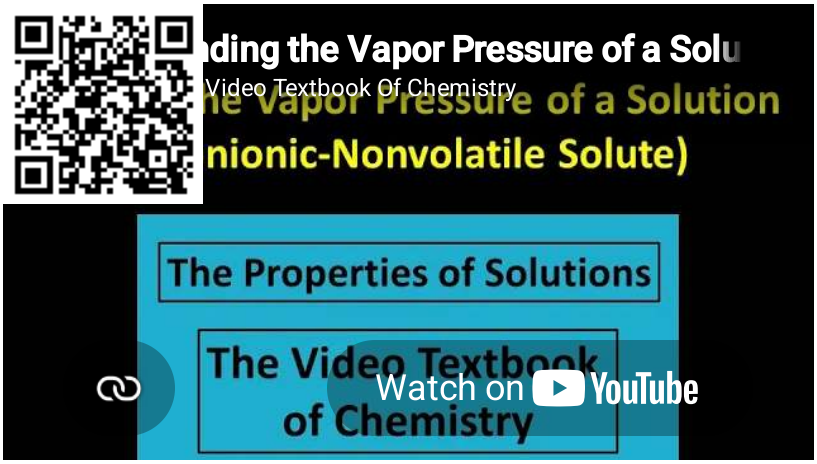
positive deviation (vapor pressure greater than predicted)

Answer c

negative deviation (vapor pressure less than predicted)



A Video Discussing Roult's Law. Video Link: Introduction to the Vapor Pressure of a Solution (Raoult's Law), YouTube(opens in new window) [youtu.be]



A Video Discussing How to find the Vapor Pressure of a Solution. Video Link: Finding the Vapor Pressure of a Solution (Nonionic-Nonvolatile Solute), YouTube(opens in new window) [youtu.be]

Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure 14.6.4). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to P = 1 atm at a higher temperature than does the curve for pure water.

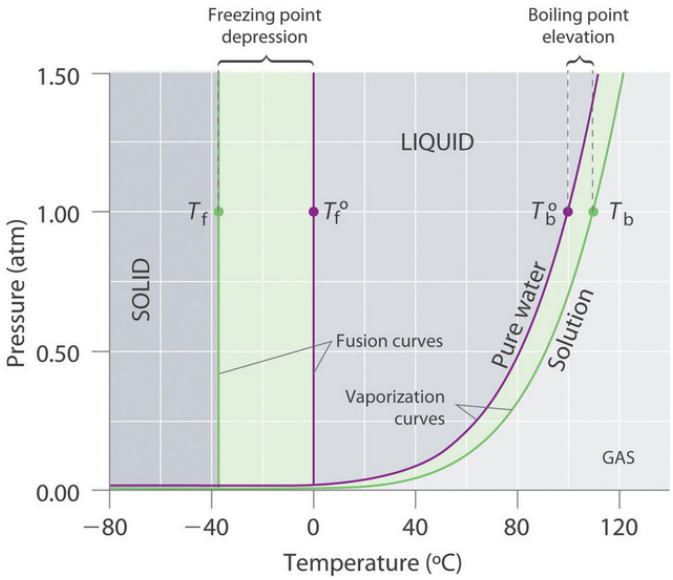


Figure 14.6.4: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution.

> *The boiling point of a solution with a nonvolatile solute is **always** greater than the boiling point of the pure solvent.*

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 14.6.5).

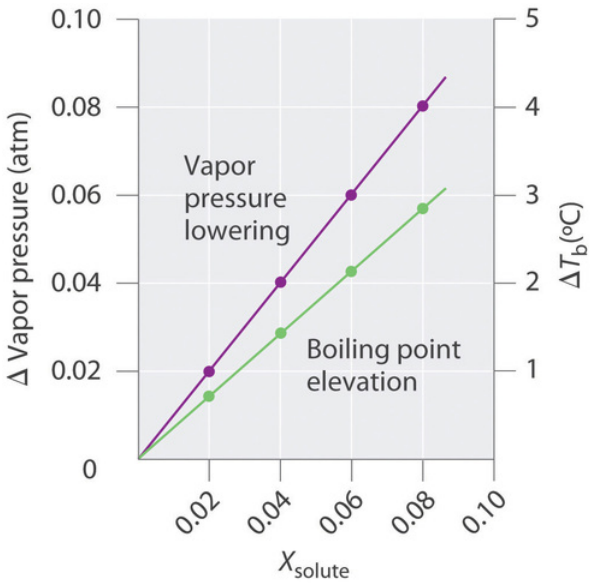


Figure 14.6.5: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute

Change in vapor pressure in atm in on the left side y axis while change in temperature is on the right side y axis. These are being plotted against mole fraction of solute.

We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{14.6.10}$$

where T_b is the boiling point of the solution and T_b^0 is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows

$$\Delta T_b = mK_b \tag{14.6.11}$$

where m is the concentration of the solute expressed in molality, and K_b is the **molal boiling point elevation constant** of the solvent, which has units of °C/m. Table 14.6.1 lists characteristic K_b values for several commonly used solvents. For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 14.6.1: 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 14.6.1, 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 14.6.3

In Example 14.6.1, 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 14.6.11 to calculate the increase in boiling point.

Solution:

From Example 14.6.1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.98\,m$$

From Equation 14.6.11, the increase in boiling point is therefore

$$\Delta T_b = mK_b = (6.98\,\cancel{m})(0.51°C/\cancel{m}) = 3.6°C$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 14.6.11 may not be valid.

Exercise 14.6.3

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

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.)



A Video Discussing Boiling Point Elevation and Freezing Point Depression. Video Link: Boiling Point Elevation and Freezing Point Depression, YouTube(opens in new window) [youtu.be] (opens in new window)

Freezing Point Depression

The phase diagram in Figure 14.6.4 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to $P = 1\ atm$ at a lower temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression (ΔT_f) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f^0 - T_f \tag{14.6.12}$$

where T_f^0 is the freezing point of the pure solvent and T_f is the freezing point of the solution.

The order of the terms is reversed compared with Equation 14.6.10 to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation 14.6.11:

$$\Delta T_f = mK_f \tag{14.6.13}$$

where m is the molality of the solution and K_f is the molal freezing point depression constant for the solvent (in units of °C/m).

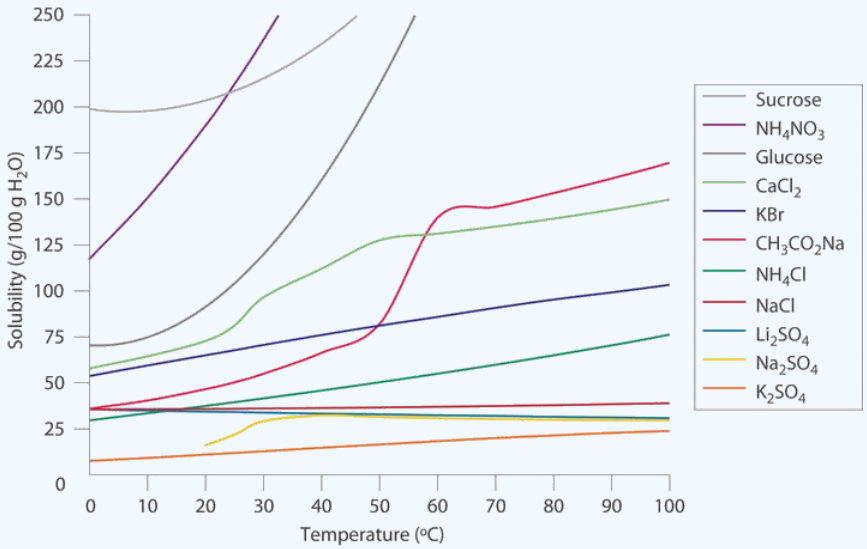
Like K_b, each solvent has a characteristic value of K_f (see Table 14.6.1). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

Example 14.6.4: Salting the Roads

In colder regions of the United States, $NaCl$ or $CaCl_2$ is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in the Figure below to estimate the concentrations of two saturated solutions at 0°C, one of $NaCl$ and one of $CaCl_2$, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.



Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.

Graph of solubility against temperature. Plots of sucrose, NH4NO3, glucose, CaCl2, KBr, CH3CO2Na, NH4Cl, NaCl, Li2SO4, Na2SO4, K2SO4.

Given: solubilities of two compounds

Asked for: concentrations and freezing points

Strategy:

A. Estimate the solubility of each salt in 100 g of water from the figure. Determine the number of moles of each in 100 g and calculate the molalities.

B. Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation 14.6.13 to calculate the freezing point depressions of the solutions.

Solution:

A From Figure above, we can estimate the solubilities of $NaCl$ and $CaCl_2$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36\ \cancel{g\ NaCl}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \cancel{g\ NaCl}}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.2\ m$$

$$m_{CaCl_2} = \left(\frac{60\ \cancel{g\ CaCl_2}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \cancel{g\ CaCl_2}}\right)\left(\frac{1000\ \cancel{g}}{1kg}\right) = 5.4\ m$$

The lower formula mass of $NaCl$ more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $CaCl_2$.

B Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of $NaCl$ and $CaCl_2$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 m = 12 m for

NaCl and 3 × 5.4 m = 16 m for $CaCl_2$. The resulting freezing point depressions can be calculated using Equation 14.6.13:

$$\text{NaCl}: \Delta T_f = mK_f = (12 \cancel{m})(1.86°C/\cancel{m}) = 22°C$$

$$\text{CaCl}_2: \Delta T_f = mK_f = (16 \cancel{m})(1.86°C/\cancel{m}) = 30°C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are −22°C and −30°C, respectively. Note that $CaCl_2$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $CaCl_2$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say −35°C), there is no point in using salt until it gets warmer

? Exercise 14.6.4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Examples 14.6.5 and 14.6.5.

Answer

−13.0°C

✓ Example 14.6.5

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 > $SrCl_2$.

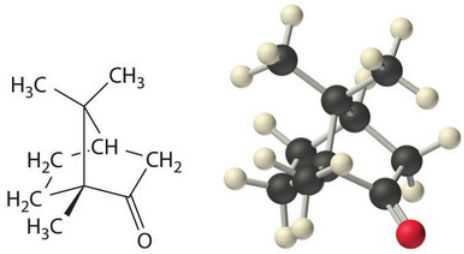
? Exercise 14.6.5

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m NaCl, 0.3 m acetic acid, 0.1 m $CaCl_2$, and 0.2 m sucrose.

Answer

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)

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure accurately and precisely. By comparing K_b and K_f values in Table 14.6.1, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of K_f (37.8°C/m), d-(+)-camphor (Table 14.6.1) is often used to determine the molar mass of organic compounds by this method.



d-(+)-Camphor

Example 14.6.6: Sulfur

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of CS_2 to create a solution whose freezing point is −113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved S_n molecules (i.e., what is the value of n?).

Given: masses of solute and solvent and freezing point

Asked for: molar mass and number of S atoms per molecule

Strategy:

A. Use Equation 14.6.12, the measured freezing point of the solution, and the freezing point of CS_2 from Table 14.6.1 to calculate the freezing point depression. Then use Equation 14.6.13 and the value of K_f from Table 14.6.1 to calculate the molality of the solution.
B. From the calculated molality, determine the number of moles of solute present.
C. Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain n, the number of sulfur atoms per mole of dissolved sulfur.

Solution:

A The first step is to calculate the freezing point depression using Equation 14.6.12:

$$\Delta T_f = T_f^0 - T_f = -112.1°C - (-113.5°C) = 1.4°C$$

Then Equation 14.6.13 gives

$$m = \frac{\Delta T_f}{K_f} = \frac{1.4°\cancel{C}}{3.74°\cancel{C}/m} = 0.37\ m$$

B The total number of moles of solute present in the solution is

$$\text{moles solute} = \left(\frac{0.37 mol}{\cancel{kg}}\right)(75.0\ g)\left(\frac{1 kg}{1000\ g}\right) = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$\text{molar mass} = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

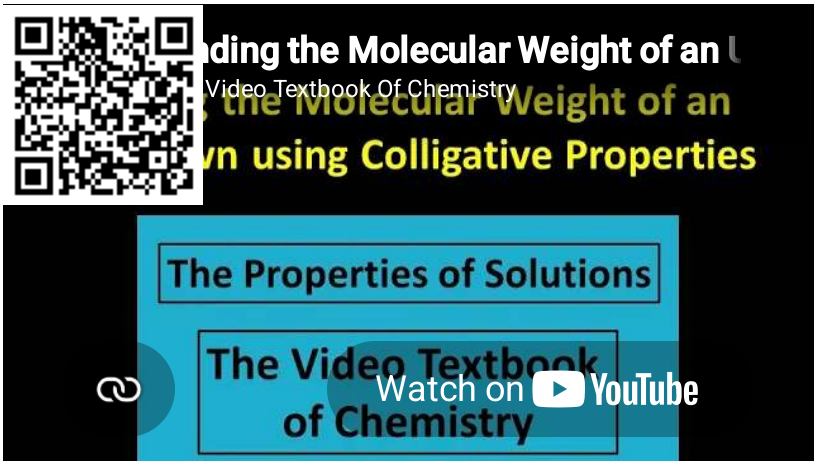
The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of S_8.

? Exercise 14.6.6

One of the byproducts formed during the synthesis of C_{60} is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of CCl_4 has a freezing point of −23.38°C. What are the molar mass and most probable formula of the substance?

Answer

847 g/mol; C_{70}



A Video Discussing how to find the Molecular Weight of an Unknown using Colligative Properties. Video Link: Finding the Molecular Weight of an Unknown using Colligative Properties, YouTube(opens in new window) [youtu.be]

Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 14.6.6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

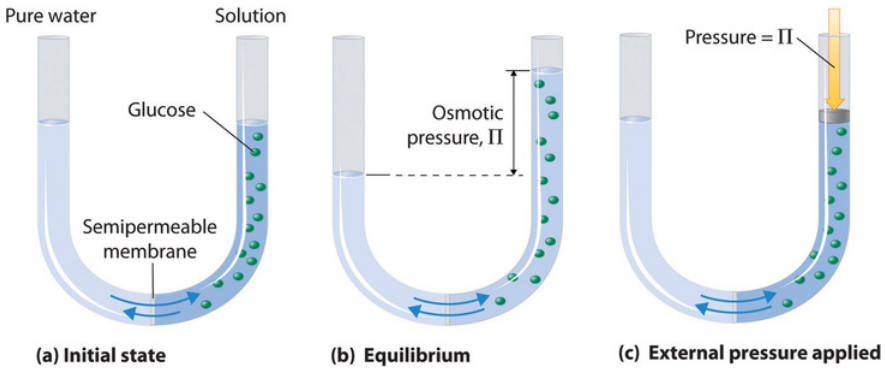


Figure 14.6.6: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT \tag{14.6.14}$$

where M is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution), R is the ideal gas constant, and T is the absolute temperature.

As shown in Example 14.6.7, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 14.6.7

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

a. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
b. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

Asked for: osmotic pressure of NaCl solution and concentration of glycerol needed

Strategy:

A. Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation 14.6.14 to calculate the osmotic pressure of the solution.
C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 14.6.14 to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

A The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$M_{NaCl} = \frac{moles\ NaCl}{\text{liter solution}}$$
$$= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \cancel{g\ solution}}\right)\left(\frac{1.02\ \cancel{g\ solution}}{1.00\ \cancel{mL}\ solution}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right)$$
$$= 0.70\ M\ \text{NaCl}$$

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 14.6.14 to calculate the osmotic pressure of the solution:

$$\Pi = MRT$$
$$= (1.4\ mol/L)\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K)$$
$$= 34\ atm$$

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 14.6.14 for the molarity corresponding to this osmotic pressure:

$$M = \frac{\Pi}{RT}$$
$$= \frac{27\ \cancel{atm}}{[0.0821(L \cdot \cancel{atm})/(\cancel{K} \cdot mol)](298\ \cancel{K})}$$
$$= 1.1\ M\ \text{glycerol}$$

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 14.6.7

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

Answer

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 14.6.7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

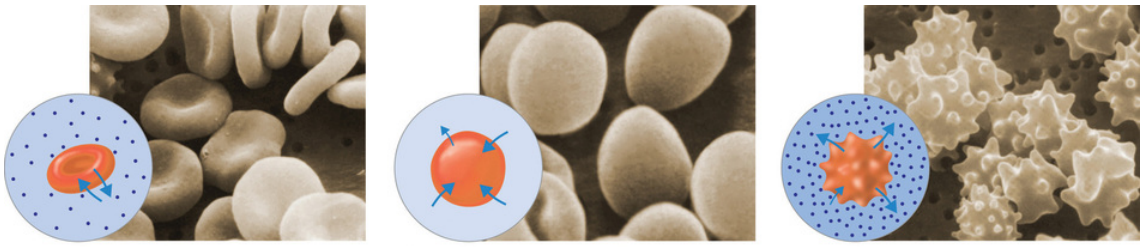


Figure 14.6.7: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function.

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure 14.6.8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

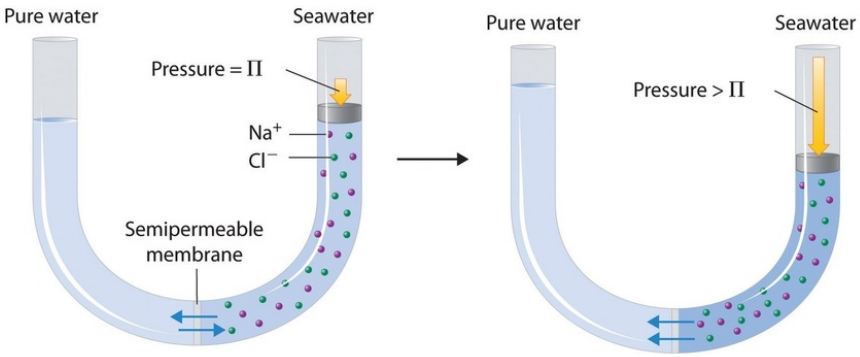
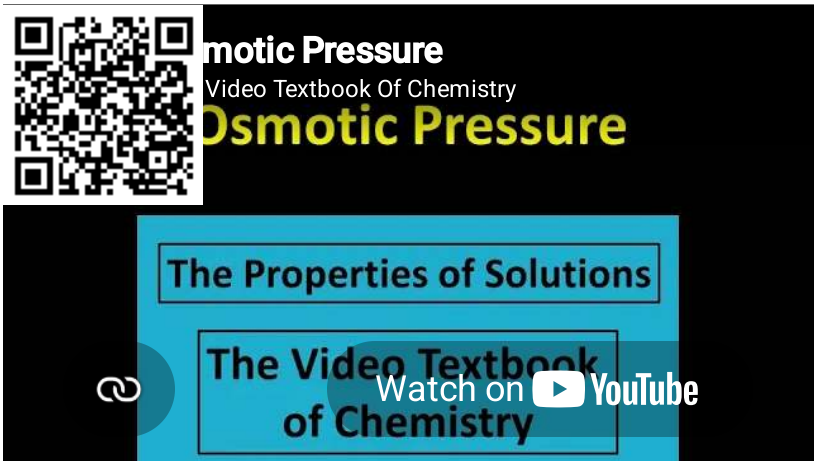


Figure 14.6.8: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely.



A Video Discussing Osmotic Pressure. Video Link: Osmotic Pressure, YouTube(opens in new window) [youtu.be] (opens in new window)

Colligative Properties of Electrolyte Solutions

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of NaCl in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of NaCl and KCl are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van't Hoff factor (i) and is defined as follows:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{14.6.15}$$

Named for Jacobus Hendricus van't Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

> *As the solute concentration increases, the van't Hoff factor decreases.*

The van't Hoff factor is therefore **a measure of a deviation from ideal behavior**. The lower the van't Hoff factor, the greater the deviation. As the data in Table 14.6.2 show, the van't Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van't Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Table 14.6.2: van't Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	i (measured)	i (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0
$NaCl$	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure 14.6.9). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+}, Al^{3+}, SO_4^{2-}, and PO_4^{3-} have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

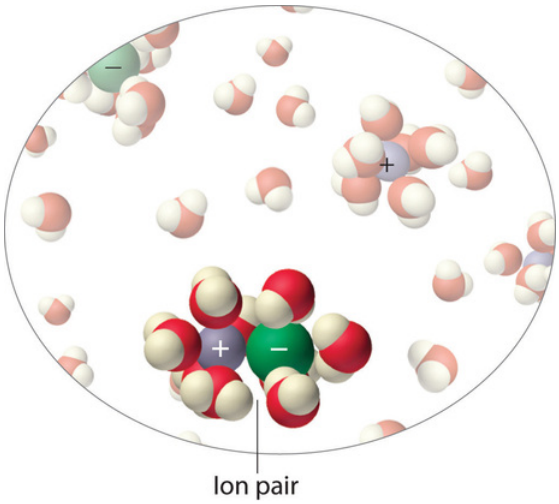


Figure 14.6.9: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

Example 14.6.8: Iron Chloride in Water

A 0.0500 M aqueous solution of $FeCl_3$ has an osmotic pressure of 4.15 atm at 25°C. Calculate the van't Hoff factor i for the solution.

Given: solute concentration, osmotic pressure, and temperature

Asked for: van't Hoff factor

Strategy:

A. Use Equation 14.6.14 to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.

B. Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 14.6.15 to calculate the van't Hoff factor.

Solution:

A If $\mathrm{FeCl_3}$ dissociated completely in aqueous solution, it would produce four ions per formula unit [Fe3+(aq) plus 3Cl−(aq)] for an effective concentration of dissolved particles of 4 × 0.0500 M = 0.200 M. The osmotic pressure would be

$$\begin{aligned}\Pi &= MRT \\ &= (0.200\ mol/L)\,[0.0821\ (L \cdot atm)/(K \cdot mol)]\,(298\ K) = 4.89\ atm\end{aligned}$$

B The observed osmotic pressure is only 4.15 atm, presumably due to ion pair formation. The ratio of the observed osmotic pressure to the calculated value is 4.15 atm/4.89 atm = 0.849, which indicates that the solution contains (0.849)(4) = 3.40 particles per mole of $\mathrm{FeCl_3}$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\left(\frac{0.0821\ (L \cdot atm)}{(K \cdot mol)}\right)(298\ K)$$

or after rearranging

$$M = 0.170 mol$$

The ratio of this value to the expected value of 0.200 M is 0.170 M/0.200 M = 0.850, which again gives us (0.850)(4) = 3.40 particles per mole of $\mathrm{FeCl_3}$ dissolved. From Equation 14.6.15, the van't Hoff factor for the solution is

$$i = \frac{3.40 \text{ particles observed}}{1 \text{ formula unit } \mathrm{FeCl_3}} = 3.40$$

? Exercise 14.6.8: Magnesium Chloride in Water

Calculate the van't Hoff factor for a 0.050 m aqueous solution of $MgCl_2$ that has a measured freezing point of −0.25°C.

Answer

2.7 (versus an ideal value of 3).



A Video Discussing the Colligative Properties in Solutions. Video Link: Colligative Properties in Solutions, YouTube(opens in new window) [youtu.be]

Summary

The colligative properties of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. Solutions that obey Raoult's law are called ideal solutions. Most real solutions exhibit positive or negative deviations from Raoult's law. The boiling

point elevation (ΔT_b) and freezing point depression (ΔT_f) of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through. In more concentrated solutions, or in solutions of salts with highly charged ions, the cations and anions can associate to form ion pairs, which decreases their effect on the colligative properties of the solution. The extent of ion pair formation is given by the van't Hoff factor (i), the ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

- **Henry's law:**

$$C = kP$$

- **Raoult's law**:

$$P_A = \chi_A P_A^0$$

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = \chi_B P_A^0$$

- **vapor pressure of a system containing two volatile components**:

$$P_{tot} = \chi_A P_A^0 + (1 - \chi_A) P_B^0$$

- **boiling point elevation**:

$$\Delta T_b = mK_b$$

- **freezing point depression:**

$$\Delta T_f = mK_f$$

- **osmotic pressure**:

$$\Pi = nRTV = MRT$$

- **van 't Hoff factor**:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}}$$

14.6: Colligative Properties- Freezing Point Depression, Boiling Point Elevation, and Osmosis is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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14.7: The Colligative Properties of Strong Electrolyte Solutions

Learning Objectives

- To understand the factors that determine the solubility of ionic compounds.

The solubility product of an ionic compound describes the concentrations of ions in equilibrium with a solid, but what happens if some of the cations become associated with anions rather than being completely surrounded by solvent? Then predictions of the total solubility of the compound based on the assumption that the solute exists solely as discrete ions would differ substantially from the actual solubility, as would predictions of ionic concentrations. In general, four situations explain why the solubility of a compound may be other than expected: ion pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH.

Ion-Pair Formation

An **ion pair** consists of a cation and an anion that are in intimate contact in solution, rather than separated by solvent (Figure 14.7.1). 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).

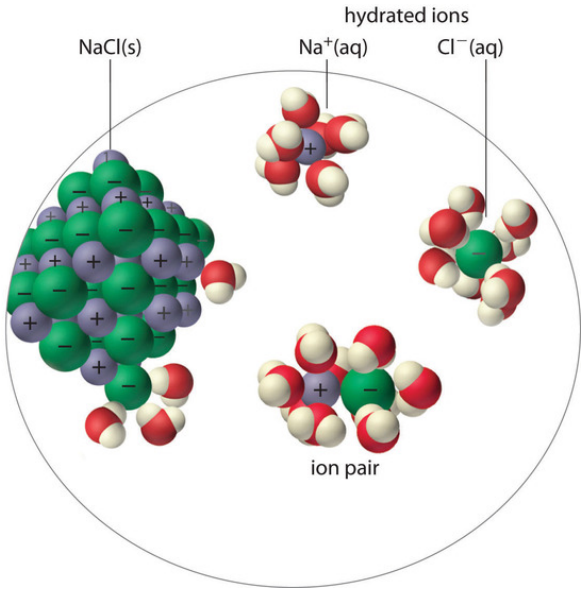


Figure 14.7.1: Ion-Pair Formation. In an ion pair, the cation and the anion are in intimate contact in solution and migrate as a single unit. They are not completely dissociated and individually surrounded by solvent molecules, as are the hydrated ions, which are free to migrate independently.

As illustrated for calcium sulfate in the following equation, a second equilibrium must be included to describe the solubility of salts that form ion pairs:

$$\mathrm{CaSO_4(s) \rightleftharpoons \underbrace{Ca^{2+} \cdot SO_4^{2-}(aq)}_{\text{ion pair}} \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)} \tag{14.7.1}$$

The ion pair is represented by the symbols of the individual ions separated by a dot, which indicates that they are associated in solution. The formation of an ion pair is a dynamic process, just like any other equilibrium, so a particular ion pair may exist only briefly before dissociating into the free ions, each of which may later associate briefly with other ions.

Ion-pair formation can have a major effect on the measured solubility of a salt. For example, the measured K_{sp} for calcium sulfate is 4.93×10^{-5} at 25°C. The solubility of $CaSO_4$ should be 7.02×10^{-3} M if the only equilibrium involved were as follows:

$$CaSO_4\,(s) \rightleftharpoons Ca^{2+}\,(aq) + SO_4^{2-}\,(aq) \tag{14.7.2}$$

In fact, the experimentally measured solubility of calcium sulfate at 25°C is 1.6×10^{-2} M, almost twice the value predicted from its K_{sp}. The reason for the discrepancy is that the concentration of ion pairs in a saturated $CaSO_4$ 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}.

> *The formation of ion pairs increases the solubility of a salt.*

Incomplete Dissociation

A molecular solute may also be more soluble than predicted by the measured concentrations of ions in solution due to incomplete dissociation. This is particularly common with weak organic acids. Although strong acids (HA) dissociate completely into their constituent ions (H^+ and A^-) in water, weak acids such as carboxylic acids do not ($K_a = 1.5 \times 10^{-5}$). However, the molecular (undissociated) form of a weak acid (HA) is often quite soluble in water; for example, acetic acid (CH_3CO_2H) is completely miscible with water. Many carboxylic acids, however, have only limited solubility in water, such as benzoic acid ($C_6H_5CO_2H$), with $K_a = 6.25 \times 10^{-5}$. Just as with calcium sulfate, we need to include an additional equilibrium to describe the solubility of benzoic acid:

$$C_6H_5CO_2H\,(s) \rightleftharpoons C_6H_5CO_2H\,(aq) \rightleftharpoons C_6H_5CO_2^-\,(aq) + H^+\,(aq)$$

In a case like this, measuring only the concentration of the ions grossly underestimates the total concentration of the organic acid in solution. In the case of benzoic acid, for example, the pH of a saturated solution at 25°C is 2.85, corresponding to $[H^+] = [C_6H_5CO_2^-] = 1.4 \times 10^{-3}$ M. The total concentration of benzoic acid in the solution, however, is 2.8×10^{-2} M. Thus approximately 95% of the benzoic acid in solution is in the form of hydrated neutral molecules—$C_6H_5CO_2H_{(aq)}$—and only about 5% is present as the dissociated ions (Figure 14.7.2).

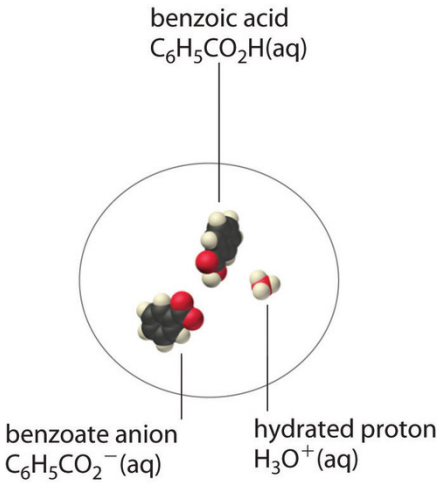


Figure 14.7.2: Incomplete Dissociation of a Molecular Solute. In a saturated solution of benzoic acid in water at 25°C, only about 5% of the dissolved benzoic acid molecules are dissociated to form benzoate anions and hydrated protons. The remaining 95% exists in solution in the form of hydrated neutral molecules. (H_2O molecules are omitted for clarity.)

Although ion pairs, such as $Ca^{2+}{\cdot}SO_4^{2-}$, and undissociated electrolytes, such as $C_6H_5CO_2H$, are both electrically neutral, there is a major difference in the forces responsible for their formation. Simple electrostatic attractive forces between the cation and the anion hold the ion pair together, whereas a polar covalent O−H bond holds together the undissociated electrolyte.

> *Incomplete dissociation of a molecular solute that is miscible with water can increase the solubility of the solute.*

Complex Ion Formation

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion {$[Cu(H_2O)_6]^{2+}$}. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure 14.7.1. 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 14.7.3: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see www.youtube.com/watch?v=IQNcLH6OZK0.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to \(\ce{Cu^{2+}}\) for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)} \qquad K_1$$

$$[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)} \qquad K_2$$

$$[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)} \qquad K_3$$

$$[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \qquad K_4$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \tag{14.7.3}$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant** (K_f). The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{14.7.4}$$

> *The formation constant (K_f) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table 14.7.1.

Table 14.7.1: Formation Constants for Selected Complex Ions in Aqueous Solution*

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

Example 14.7.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 14.7.3 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (Equation 14.7.4) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}$ (aq), as shown in Equation 14.7.3. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5 \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65 \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define *x* as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is −*x*, and the change in the concentration of ammonia is +4*x*, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

Solutions to Example 17.5.1

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
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 (Equation 14.7.4) and assuming that $x \ll 0.0846$, which allows us to remove *x* from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13}$$

$$x = 2.1 \times 10^{-14}$$

The value of x indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore $2.1 \times 10^{-14} M$.

? Exercise 14.7.1

The ferrocyanide ion $[Fe(CN)_6]^{4-}$ is very stable, with a $K_f = 1 \times 10^{35}$. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer

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 ×

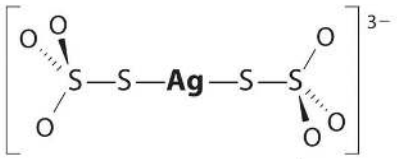
10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the 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:

$$\mathrm{AgBr\,(s) \rightleftharpoons Ag^+\,(aq) + Br^-\,(aq)}$$

with $K_{sp} = 5.35 \times 10^{-13}$ at 25°C.

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$\mathrm{Ag^+\,(aq) + 2\,S_2O_3^{2-}\,(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}\,(aq)}$$

with $K_f = 2.9 \times 10^{13}$.

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$\mathrm{AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)} \quad K_{sp} = 5.35 \times 10^{-13} \tag{14.7.5}$$

$$\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)} \quad K_f = 2.9 \times 10^{13} \tag{14.7.6}$$

$$\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)} \quad K = K_{sp}K_f = 15 \tag{14.7.7}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

Example 14.7.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.

B. Calculate the concentration of Ag^+ in the KCl solution.

C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.

D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let x equal the solubility of AgCl, then at equilibrium [Ag+] = $[Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77 \times 10^{-10}$$
$$x = 1.33 \times 10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77 \times 10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.77 \times 10^{-10} \tag{14.7.8}$$
$$Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^- \quad K_f = 1.1 \times 10^5 \tag{14.7.9}$$
$$AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^- \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{14.7.10}$$

D If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x << 1.0$,

$$K = \frac{[AgCl_2^-]}{[Cl^-]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

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 14.7.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water

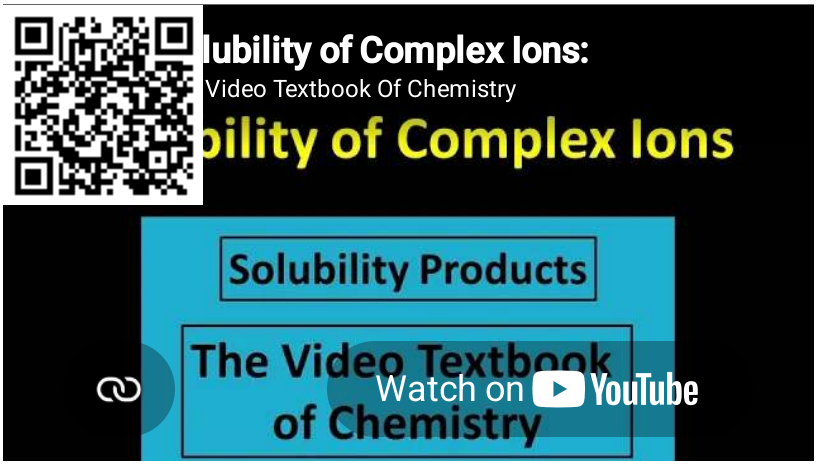
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

Answer

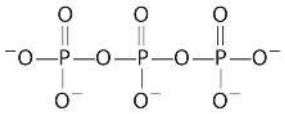
a. 1.9×10^{-10} M

b. 1.4 M



Solubility of Complex Ions: Solubility of Complex Ions(opens in new window) [youtu.be]

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:

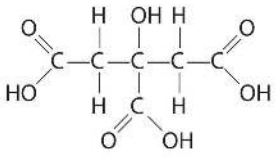


triphosphate

$$Ca^{2+}(aq) + O_3POPO_4^{4-}(aq) \rightleftharpoons [Ca(O_3POPO_3)]^{2-}(aq) \tag{14.7.11}$$

with $K_f = 4 \times 10^4$.

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



Citric acid,
a hydroxy polycarboxylic acid

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as "MRI contrast agents." Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and

allows doctors to “see” each of these separately (Figure 14.7.4). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as DTPA^{5-} (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

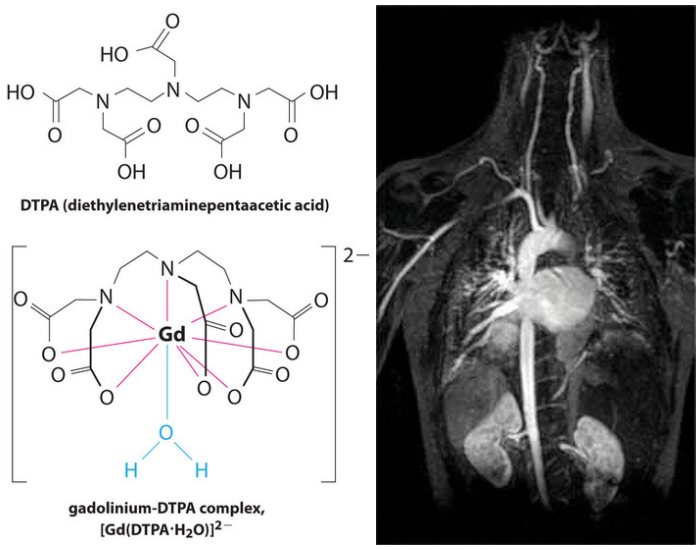


Figure 14.7.4: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Summary

Ion-pair formation, the incomplete dissociation of molecular solutes, the formation of complex ions, and changes in pH all affect solubility. There are four explanations why the solubility of a compound can differ from the solubility indicated by the concentrations of ions: (1) ion pair formation, in which an anion and a cation are in intimate contact in solution and not separated by solvent, (2) the incomplete dissociation of molecular solutes, (3) the formation of complex ions, and (4) changes in pH. An ion pair is held together by electrostatic attractive forces between the cation and the anion, whereas incomplete dissociation results from intramolecular forces, such as polar covalent O–H bonds.

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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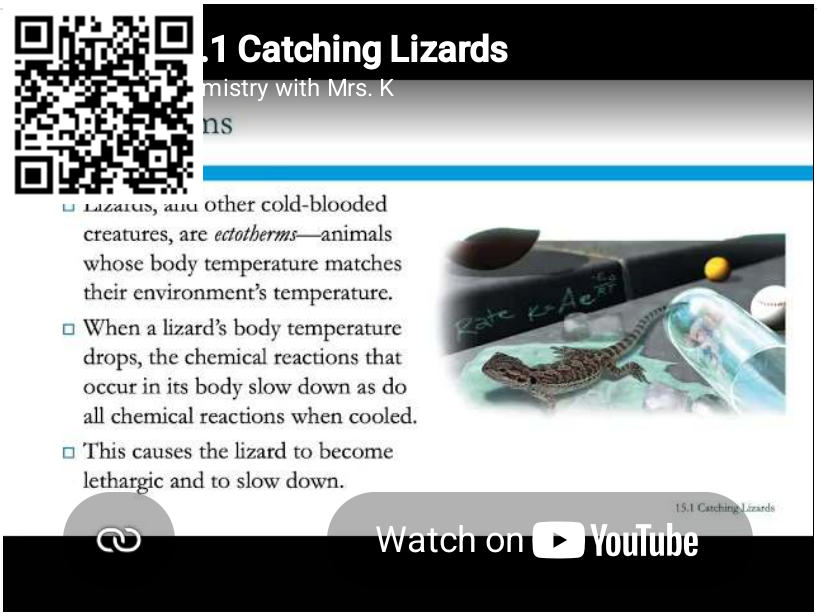
CHAPTER OVERVIEW

15: Chemical Kinetics

15.1: Catching Lizards
15.2: Rates of Reaction and the Particulate Nature of Matter
15.3: Defining and Measuring the Rate of a Chemical Reaction
15.4: The Rate Law- The Effect of Concentration on Reaction Rate
15.5: The Integrated Rate Law- The Dependence of Concentration on Time
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15.8: Catalysis

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15.1: Catching Lizards



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15.2: Rates of Reaction and the Particulate Nature of Matter

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.

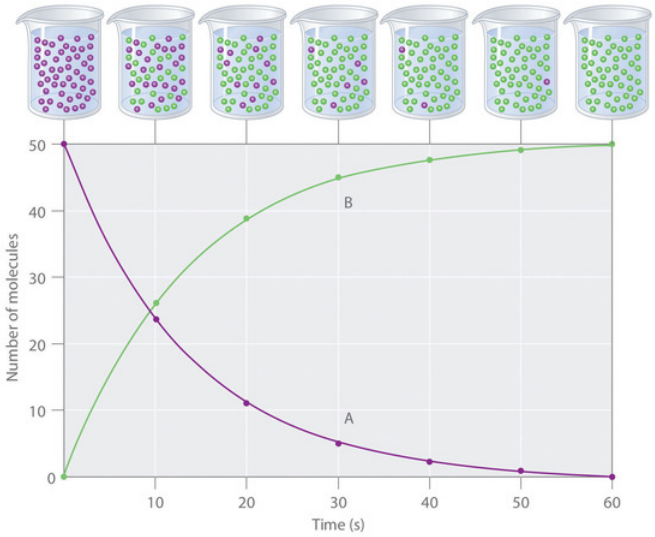


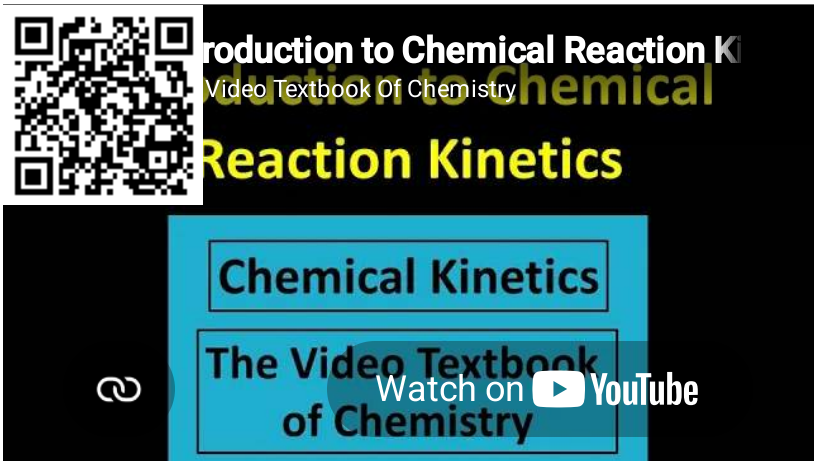
Figure 15.2.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 15.2.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 15.2.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{15.2.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 15.2.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*



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 15.2.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure 15.2.2.

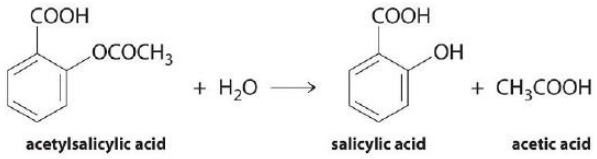


Figure 15.2.2: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 15.2.1 and are shown in the graph in Figure 15.2.3.

Table 15.2.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
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 15.2.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

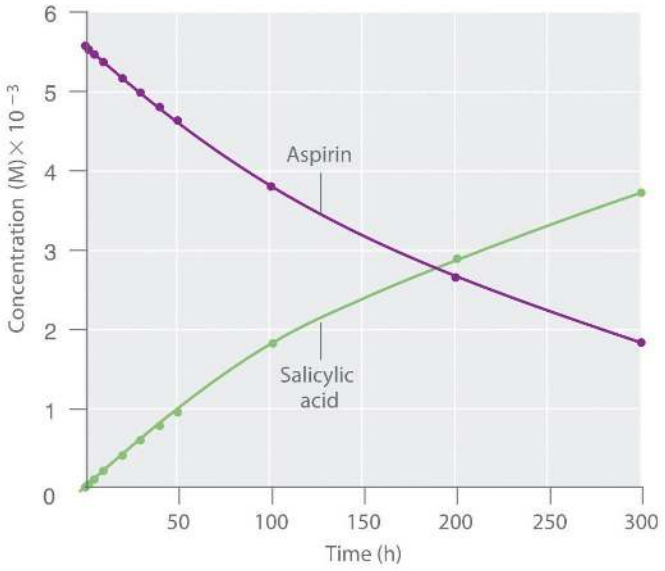


Figure 15.2.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= \frac{0.040 \times 10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0 \times 10^{-5}\text{ M/h}\end{aligned}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= -\frac{(5.51 \times 10^{-3}\text{ M}) - (5.55 \times 10^{-3}\text{ M})}{2.0\text{ h}} \\ &= 2 \times 10^{-5}\text{ M/h}\end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 15.2.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\begin{aligned}\text{rate}_{(t=200-300\text{h})} &= \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\text{ h} - 200\text{ h}} \\ &= -\frac{(3.73 \times 10^{-3}\text{ M}) - (2.91 \times 10^{-3}\text{ M})}{100\text{ h}} \\ &= 8.2 \times 10^{-6}\text{ M/h}\end{aligned}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{15.2.2}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{15.2.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 15.2.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 15.2.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{15.2.4}$$

Example 15.2.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

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:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Exercise 15.2.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

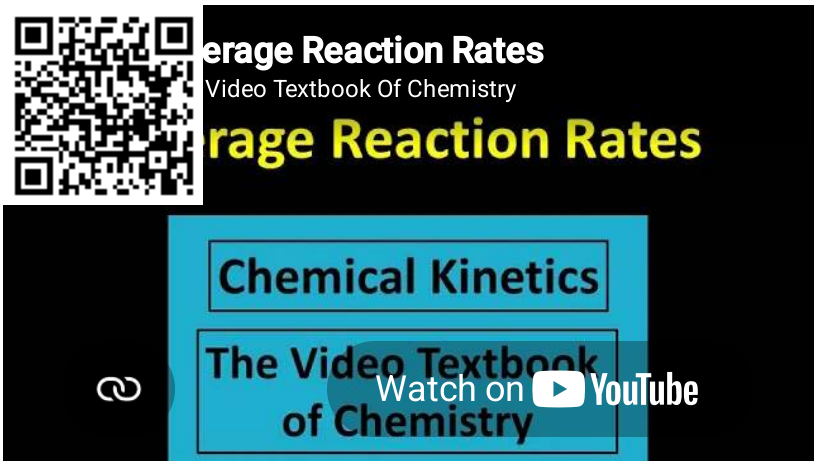
$$\text{rate} = -\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{\Delta[\text{SO}_2]}{2\Delta t} = \frac{\Delta[\text{SO}_3]}{2\Delta t}$$

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.*



Example 15.2.2: Decomposition Reaction II

Using the reaction shown in Example 15.2.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

calculate the reaction rate from the following data taken at 56°C:

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example 15.2.1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 15.2.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

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,

$$\text{rate} = -\frac{\Delta[N_2O_5]}{2\Delta t} = -\frac{[N_2O_5]_{600} - [N_2O_5]_{240}}{2(600\text{ s} - 240\text{ s})}$$

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:

$$\text{rate} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{[NO_2]_{600} - [NO_2]_{240}}{4(600\text{ s} - 240\text{ s})} = \frac{0.0699\text{ M} - 0.0314\text{ M}}{4(360\text{ s})} = 2.67 \times 10^{-5}\text{ M/s}$$

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:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{[O_2]_{600} - [O_2]_{240}}{600\text{ s} - 240\text{ s}} = \frac{0.0175\text{ M} - 0.00792\text{ M}}{360\text{ s}} = 2.66 \times 10^{-5}\text{ M/s}$$

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 15.2.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

9.0×10^{-6} M/s

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:

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

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15.3: Defining and Measuring the Rate of a Chemical Reaction



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15.4: The Rate Law- The Effect of Concentration on Reaction Rate

Learning Objectives

- To understand the meaning of the rate law.

The factors that affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A **differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt). In contrast, an **integrated rate law** describes the reaction rate in terms of the initial concentration ($[R]_0$) and the measured concentration of one or more reactants ([R]) after a given amount of time (t); integrated rate laws are discussed in more detail later. The integrated rate law is derived by using calculus to integrate the differential rate law. Whether using a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).

Reaction Orders

For a reaction with the general equation:

$$aA + bB \rightarrow cC + dD \tag{15.4.1}$$

the experimentally determined rate law usually has the following form:

$$\text{rate} = k[A]^m[B]^n \tag{15.4.2}$$

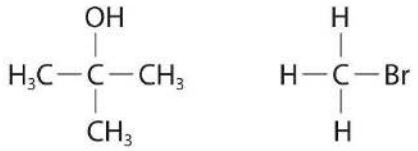
The proportionality constant (*k*) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of *k*, however, does not change as the reaction progresses under a given set of conditions.

> *Under a given set of conditions, the value of the rate constant does **not** change as the reaction progresses.*

The reaction rate thus depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers *m* and *n*, respectively. The values of *m* and *n* are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; *m* and *n* need not be integers. For example, Equation 15.4.2 tells us that Equation 15.4.1 is m^{th} order in reactant A and n^{th} order in reactant B. It is important to remember that *n* and *m* are not related to the stoichiometric coefficients *a* and *b* in the balanced chemical equation and must be determined **experimentally**. The overall reaction order is the sum of all the exponents in the rate law: *m* + *n*.

> *The orders of the reactions (e.g. n and m) are **not** related to the stoichiometric coefficients in the balanced chemical (e.g., a and b).*

To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone.



t-butanol methyl bromide

This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{15.4.3}$$

Combining the rate expression in Equation 15.4.2 with the definition of average reaction rate

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t}$$

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{15.4.4}$$

Inserting the identities of the reactants into Equation 15.4.4 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(\text{CH}_3)_3\text{CBr}]}{\Delta t} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n \tag{15.4.5}$$

Experiments to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Therefore, m and n in Equation 15.4.4 are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{15.4.6}$$

Because the exponent for the reactant is 1, the reaction is first order in $(CH_3)_3CBr$. It is zeroth order in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus, the overall reaction order is 1 + 0 = 1. The reaction orders state in practical terms that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when working with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law must be determined experimentally.) Experimental data show that *k* has the value 5.15×10^{-4} s^{-1} at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$\text{rate} = -\frac{\Delta[\text{CH}_3\text{Br}]}{\Delta t} = k'[\text{CH}_3\text{Br}] \tag{15.4.7}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 15.4.7 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus, methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often alter reaction conditions to study the mechanics of a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. In contrast, for methyl bromide, the differential rate law becomes

$$\text{rate} = k''[CH_3Br][OH^-]$$

with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, providing clues as to how the reactions differ on a molecular level.

Example 15.4.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g)$$

is second order in $\mathrm{NO_2}$ and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\mathrm{NO_2}]^m[\mathrm{CO}]^n$$

The reaction is second order in $\mathrm{NO_2}$; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[\mathrm{NO_2}]^2[\mathrm{CO}]^0 = k[\mathrm{NO_2}]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[\mathrm{CO}]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of $\mathrm{NO_2}$. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise 15.4.1A

The rate law for the reaction:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g)$$

has been experimentally determined to be $rate = k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2
- order in $\mathrm{H_2}$ = 1
- overall order = 3

Exercise 15.4.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol ($\mathrm{CH_3OH}$) and ethyl acetate ($\mathrm{CH_3CH_2OCOCH_3}$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH} + \mathrm{CH_3CH_2OCOCH_3} \longrightarrow \mathrm{CH_3OCOCH_3} + \mathrm{CH_3CH_2OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[\mathrm{CH_3OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in $\mathrm{CH_3OH}$ = 1
- order in $\mathrm{CH_3CH_2OCOCH_3}$ = 0
- overall order = 1

Example 15.4.2: Differential Rate Laws

Below are three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

a. $$2\mathrm{HI(g)} \xrightarrow{\mathrm{Pt}} \mathrm{H_2(g)} + \mathrm{I_2(g)}$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{HI}]}{\Delta t}\right) = k[\mathrm{HI}]^2$$

b. $$2\mathrm{N_2O(g)} \xrightarrow{\Delta} 2\mathrm{N_2(g)} + \mathrm{O_2(g)}$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{N_2O}]}{\Delta t}\right) = k$$

c. $$\mathrm{cyclopropane(g)} \rightarrow \mathrm{propane(g)}$$
$$\text{rate} = -\frac{\Delta[\mathrm{cyclopropane}]}{\Delta t} = k[\mathrm{cyclopropane}]$$

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)]:

$$k\mathrm{M}^2 = \frac{\mathrm{M}}{\mathrm{s}}k = \frac{\mathrm{M/s}}{\mathrm{M}^2} = \frac{1}{\mathrm{M \cdot s}} = \mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$$

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·s^{-1} = M/s.

B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

C Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

? Exercise 15.4.2

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

a. $\mathrm{CH_3N{=}NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)}$ $\quad \text{rate} = -\dfrac{\Delta[\mathrm{CH_3N{=}NCH_3}]}{\Delta t}$ (15.4.8)

$= k[\mathrm{CH_3N{=}NCH_3}]$ (15.4.9)

b. $\mathrm{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)}$ $\quad \text{rate} = -\dfrac{\Delta[\mathrm{F_2}]}{\Delta t} = -\dfrac{1}{2}\left(\dfrac{\Delta[\mathrm{NO_2}]}{\Delta t}\right)$ (15.4.10)

$= k[\mathrm{NO_2}][\mathrm{F_2}]$ (15.4.11)

Answer a

$\mathrm{s^{-1}}$; first order in $\mathrm{CH_3N{=}NCH_3}$; first order overall; doubling $[\mathrm{CH_3N{=}NCH_3}]$ will double the reaction rate.

Answer b

$\mathrm{M^{-1}{\cdot}s^{-1}}$; first order in $\mathrm{NO_2}$, first order in $\mathrm{F_2}$; second order overall; doubling $[\mathrm{NO_2}]$ will double the reaction rate.

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding **reaction mechanisms** can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine k and the exponents m and n in the following equation:

$$\text{rate} = k[A]^m[B]^n \tag{15.4.12}$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments. Rate data for a hypothetical reaction of the type $A + B \rightarrow products$ are given in Table 15.4.1.

Table 15.4.1: 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 15.4.12. We can obtain m or n directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 15.4.3.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\mathrm{A}_1]^m[\mathrm{B}_1]^n}{k[\mathrm{A}_3]^m[\mathrm{B}_3]^n}$$

Inserting the appropriate values from Table 15.4.3,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{34 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[1.00\ \text{M}]^m[0.50\ \text{M}]^n}$$

Because 1.00 to any power is 1, $[1.00\ \text{M}]^m = 1.00\ \text{M}$. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for m.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for n.

$$\frac{\text{rate}_1}{\text{rate}_5} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_5]^m[\text{B}_5]^n}$$

Substituting the appropriate values from Table 15.4.3,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{8.5 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[0.50\ \text{M}]^m[1.00\ \text{M}]^n}$$

Canceling leaves $1.0 = [0.50]^n$, which gives $n = 0$; that is, the reaction is zeroth order in B. The experimentally determined rate law is therefore

$$\text{rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of Table 15.4.3 into the experimentally determined rate law and solving for k. Using Experiment 2, we obtain

$$19 \times 10^{-3}\ \text{M/min} = k(0.75\ \text{M})^2$$

$$3.4 \times 10^{-2}\ \text{M}^{-1}\cdot\text{min}^{-1} = \text{k}$$

You should verify that using data from any other row of Table 15.4.1 gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

Example 15.4.3

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with O_2 to give NO_2, which then reacts rapidly with water to give nitrous acid and nitric acid:

$$2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2 \xrightarrow{\text{H}_2\text{O}} \text{HNO}_2 + \text{HNO}_3$$

These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Determine the rate law for the reaction and calculate the rate constant.

rate law for the reaction and calculate the rate constant.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:

A. Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.

B. Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for *k*.

Solution

A Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$\text{rate} = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{7.98 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0125\ \text{M})} = 1.16 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1}$$

Alternatively, using Experiment 2 gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{15.9 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0250\ \text{M})} = 1.15 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1}$$

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 15.4.3

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O^{2-}_{8(aq)} + 3I^-_{(aq)} \rightarrow 2SO^{2-}_{4(aq)} + I^-_{3(aq)}$$

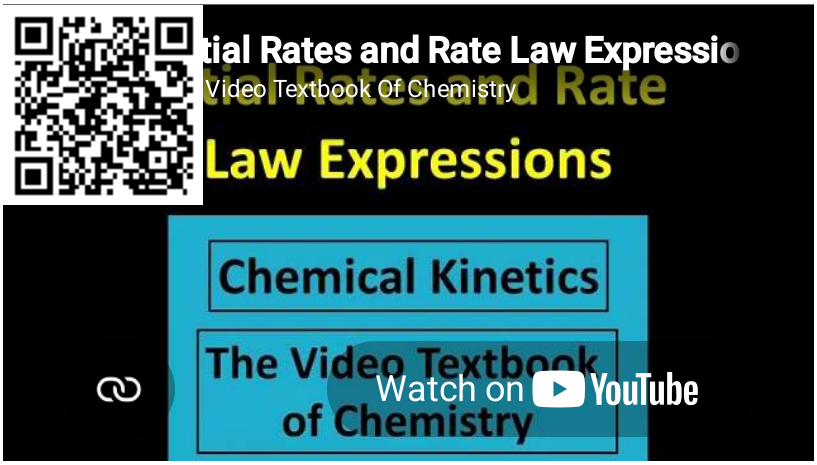
The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

kinetics data for this reaction at 25°C.

Experiment	$[S_2O_8^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer:

rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ \text{M}^{-1}\cdot\text{s}^{-1}$



A Video Discussing Initial Rates and Rate Law Expressions. Video Link: Initial Rates and Rate Law Expressions(opens in new window) [youtu.be]

Summary

The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a differential rate law, describing the change in reactant or product concentrations as a function of time, or as an integrated rate law, describing the actual concentrations of reactants or products as a function of time. The rate constant (k) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The exponent to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

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15.5: The Integrated Rate Law- The Dependence of Concentration on Time

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{15.5.1}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.

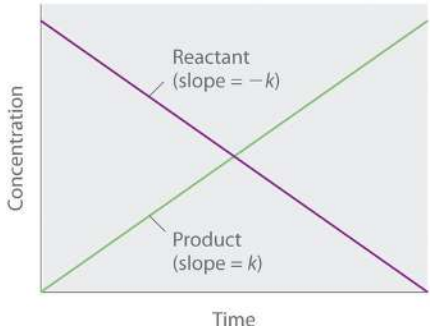


Figure 15.5.1: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.
Graph of concentration against time. The reactant is in purple and has a slope of minus k. The product is in green and has a slope of positive k.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{15.5.2}$$

where $[A]_0$ is the initial concentration of reactant A. Equation 15.5.2 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.)

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g) \tag{15.5.3}$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k \tag{15.5.4}$$

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 15.5.2, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

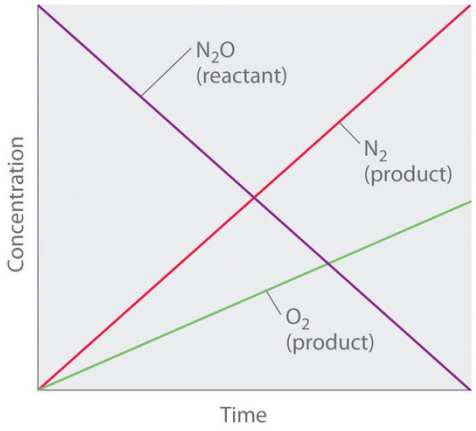


Figure 15.5.2: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N2O is the reactiant is graphed in purple. O2 is one of the products and is graphed in green. The second product is N2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is



Figure 15.5.2

where \ce{NAD^{+}} (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (Figure 15.5.3*a*). 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 15.5.3).

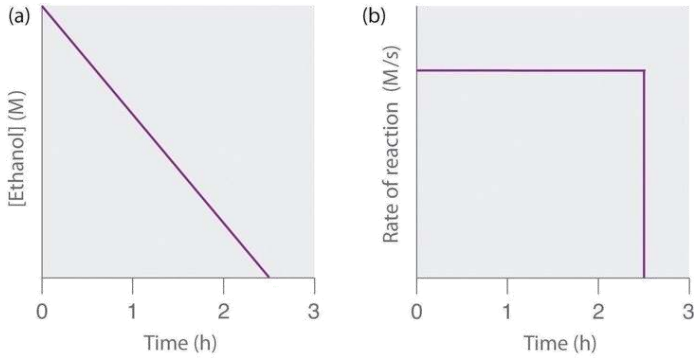


Figure 15.5.3: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{15.5.5}$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{15.5.6}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 15.5.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 15.5.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln [A]_0 - kt \tag{15.5.7}$$

Because Equation 15.5.7 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = \ln[A]$ and $b = \ln [A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln [A]_0$. Either the differential rate law (Equation 15.5.5) or the integrated rate law (Equation 15.5.7) can be used to determine whether a particular reaction is first order.

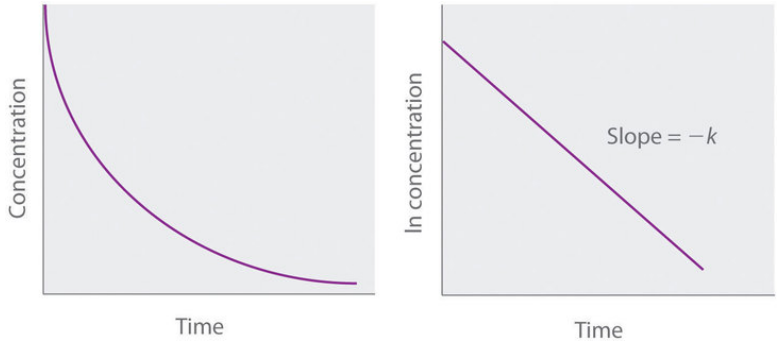


Figure 15.5.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin. Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

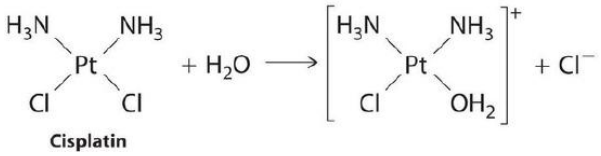


Figure 15.5.5: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 15.5.5 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 15.5.4 have been studied extensively to find ways of maximizing the concentration of the active species.

> *If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.*

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 15.5.1. 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.

Table 15.5.1: 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}

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 15.5.1 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 = $k[\text{cisplatin}]^1$. 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 15.5.1. For example, substituting the values for Experiment 3 into Equation 15.5.5,

$$3.6 \times 10^{-5}\ \text{M/min} = k(0.024\ \text{M})$$

$$1.5 \times 10^{-3}\ \text{min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example 15.5.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$\text{CH}_3\text{CH}_2\text{Cl}\,(\text{g}) \xrightarrow{\Delta} \text{HCl}\,(\text{g}) + \text{C}_2\text{H}_4\,(\text{g})$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

data for the reaction at 650°C

Experiment	$[CH_3CH_2Cl]_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.

B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8}\ \text{M/s} = k(0.010\ \text{M})$$

$$1.6 \times 10^{-6}\ \text{s}^{-1} = k$$

Exercise 15.5.1

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.

Data for the reaction at 320°C

Experiment	$[SO_2Cl_2]_0$ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer

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. Figure 15.5.6*a* shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

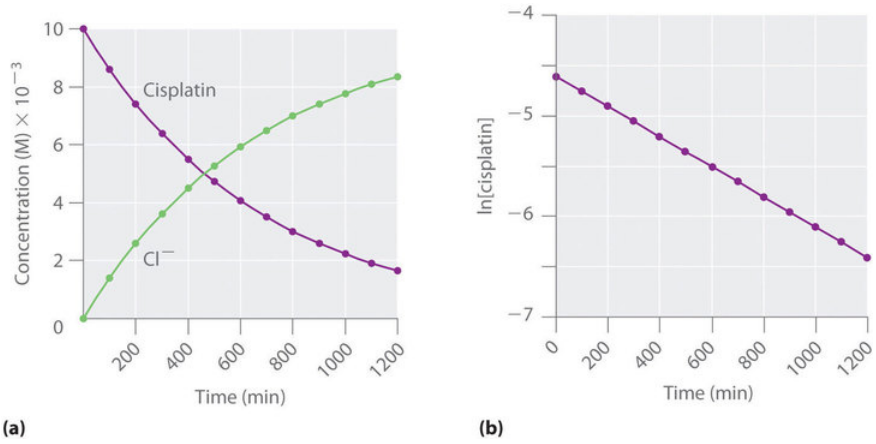


Figure 15.5.6: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure 15.5.6. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 15.5.6 for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

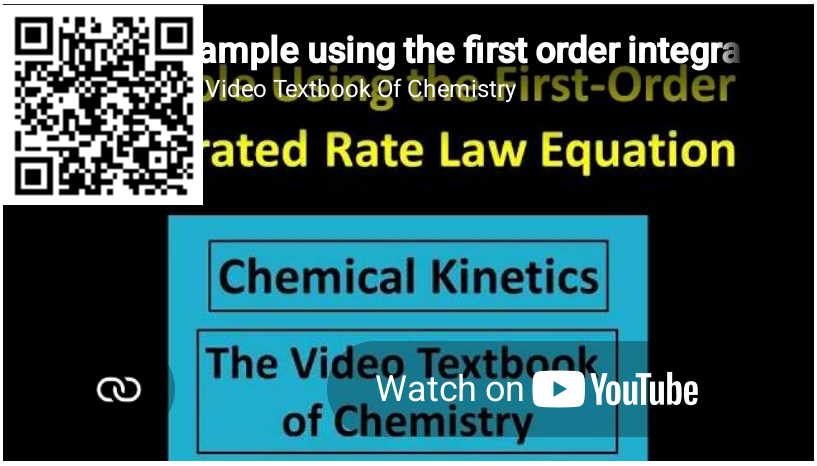
$$\text{slope} = \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000\ \text{min} - 100\ \text{min}}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000\ \text{min} - 100\ \text{min}} = \frac{-6.12 - (-4.76)}{900\ \text{min}} = -1.51 \times 10^{-3}\ \text{min}^{-1}$$

$$k = 1.5 \times 10^{-3}\ \text{min}^{-1}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure 15.5.6 are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.



Video Example Using the First-Order Integrated Rate Law Equation:

Example Using the First-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Example 15.5.2

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 ($k = 1.6 \times 10^{-6}\ s^{-1}$) ?

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 15.5.6) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6}\ s^{-1}$, we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$\begin{aligned}[CH_3CH_2Cl]_{10\ h} &= [CH_3CH_2Cl]_0 e^{-kt} \\ &= 0.0200\ M(e^{-(1.6\times10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)]}) \\ &= 0.0189\ M\end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 15.5.7):

$$\begin{aligned}\ln [CH_3CH_2Cl]_{10\ h} &= \ln [CH_3CH_2Cl]_0 - kt \\ &= \ln 0.0200 - (1.6 \times 10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)] \\ &= -3.912 - 0.0576 = -3.970 \\ [CH_3CH_2Cl]_{10\ h} &= e^{-3.970}\ M \\ &= 0.0189\ M\end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 15.5.7 gives the following:

$$\ln [CH_3CH_2Cl]_t = \ln [CH_3CH_2Cl]_0 - kt$$

$$kt = \ln [CH_3CH_2Cl]_0 - \ln [CH_3CH_2Cl]_t = \ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}$$

$$t = \frac{1}{k}\left(\ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}\right) = \frac{1}{1.6 \times 10^{-6}\ \text{s}^{-1}}\left(\ln \frac{0.0200\ \text{M}}{0.0050\ \text{M}}\right)$$

$$= \frac{\ln 4.0}{1.6 \times 10^{-6}\ \text{s}^{-1}} = 8.7 \times 10^5\ \text{s} = 240\ \text{h} = 2.4 \times 10^2\ \text{h}$$

? Exercise 15.5.2

In the exercise in Example 15.5.1, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C.

a. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C.
b. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form

$$2\,A \longrightarrow \text{products}\cdot$$

A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\text{rate} = -\frac{\Delta[A]}{2\Delta t} = k[A]^2 \tag{15.5.8}$$

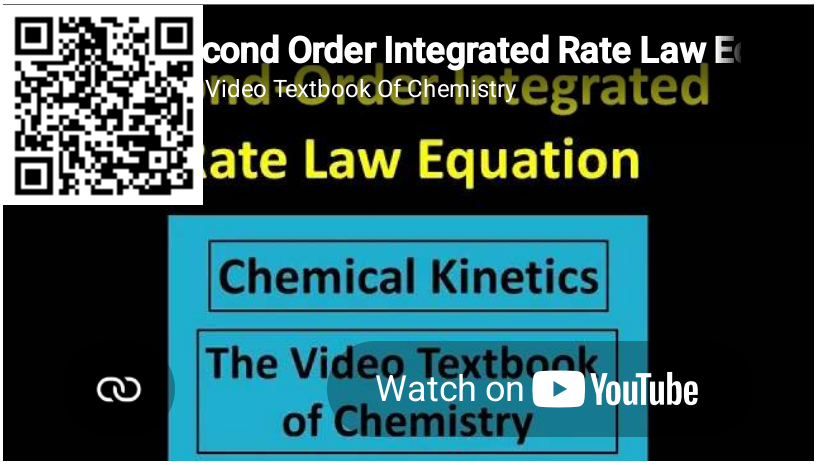
Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}{\cdot}s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \tag{15.5.9}$$

Because Equation 15.5.9 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of 1/[A] versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

> *Second-order reactions generally have the form 2A → products or A + B → products.*



Video Discussing the Second-Order Integrated Rate Law Equation: Second-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

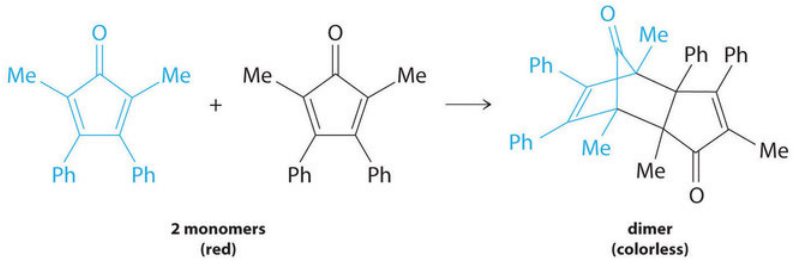


Figure 15.5.7

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 15.5.8) or the integrated rate law (Equation 15.5.9).

Table 15.5.2: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 15.5.2. From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5}\ \text{M/min}}{1.8 \times 10^{-5}\ \text{M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3}\ \text{M}}{2.0 \times 10^{-3}\ \text{M}} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 15.5.8 and the data from any row in Table 15.5.2, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{15.5.10}$$

$$8.0 \times 10^{-5}\ \text{M/min} = k(4.4 \times 10^{-3}\ \text{M})^2 \tag{15.5.11}$$

$$4.1\ \text{M}^{-1} \cdot \text{min}^{-1} = k \tag{15.5.12}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure 15.5.8*a*. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in Figure 15.5.8*b*. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1\ \text{M}^{-1}\cdot\text{min}^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

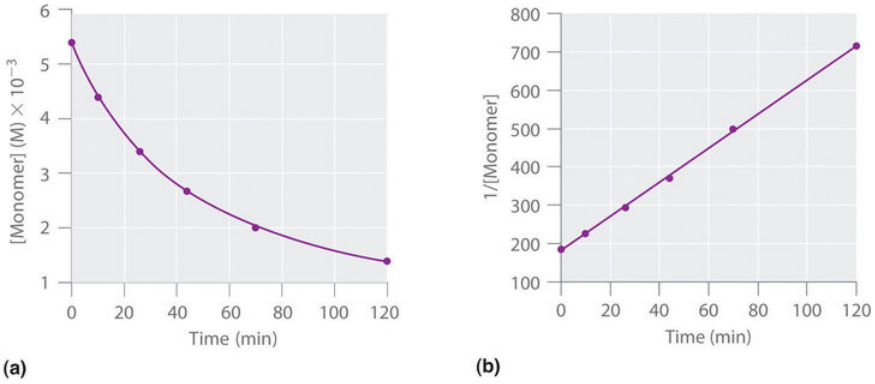


Figure 15.5.8: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

Example 15.5.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2\text{NO}_2(\text{g}) \xrightarrow{\Delta} 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO2

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A. From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.

B. Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\begin{aligned} \text{rate} &= k[\text{NO}_2]^2 \\ 5.40 \times 10^{-5}\ \text{M/s} &= k(0.010\ \text{M})^2 \\ 0.54\ \text{M}^{-1} \cdot \text{s}^{-1} &= k \end{aligned}$$

? Exercise 15.5.3

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$$2HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Some initial rate data at 25°C

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer

second order in HO_2; $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/(reactant concentration) versus time is linear, then the reaction is second order.

Example 15.5.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 15.5.9) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A. Given k, t, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].
B. Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for t.

Solution

A We know k and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at t = 1 h (3600 s). Substituting the appropriate values into Equation 15.5.9,

$$\begin{aligned}\frac{1}{[NO_2]_{3600}} &= \frac{1}{[NO_2]_0} + kt \\ &= \frac{1}{0.056\ M} + [(0.54\ M^{-1}\cdot s^{-1})(3600\ s)] \\ &= 2.0 \times 10^3\ M^{-1}\end{aligned}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

B In this case, we know k and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ M) = 0.0056$ M. To do this, we solve Equation 15.5.9 for t, using the concentrations given.

$$\begin{aligned}t &= \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k} \\ &= \frac{(1/0.0056\ M) - (1/0.056\ M)}{0.54\ M^{-1}\cdot s^{-1}} \\ &= 3.0 \times 10^2\ s = 5.0\ min\end{aligned}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise 15.5.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 15.5.9) and the rate constant calculated in the exercise in Example 15.5.3.

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:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = k[\text{A}][\text{B}]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k$$

$$[A] = [A]_0 - kt$$

- **first-order reaction**:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

$$[A] = [A]_0 e^{-kt}$$

$$\ln[A] = \ln[A]_0 - kt$$

- **second-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$$

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15.6: The Effect of Temperature on Reaction Rate

Learning Objectives

- To understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. The collision model explains why chemical reactions often occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates. Before delving into the relationship between temperature and reaction rate, we must discuss three microscopic factors that influence the observed macroscopic reaction rates.

Microscopic Factor 1: Collisional Frequency

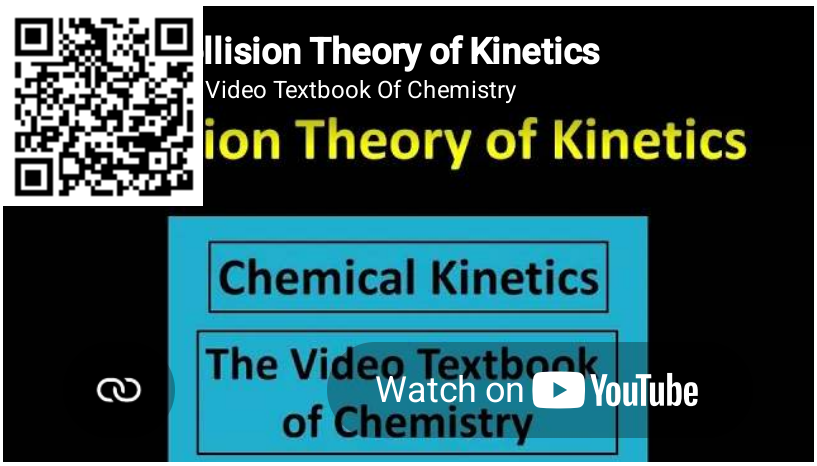
Central to collision model is that a chemical reaction can occur only when the reactant molecules, atoms, or ions collide. Hence, the observed rate is influence by the frequency of collisions between the reactants. The **collisional frequency** is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system. While deriving the collisional frequency (Z_{AB}) between two species in a gas is straightforward, it is beyond the scope of this text and the equation for collisional frequency of A and B is the following:

$$Z_{AB} = N_A N_B \left(r_A + r_B\right)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \tag{15.6.1}$$

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 15.6.1 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).



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 15.6.1 shows a plot of the rate constant of the reaction of NO with 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.

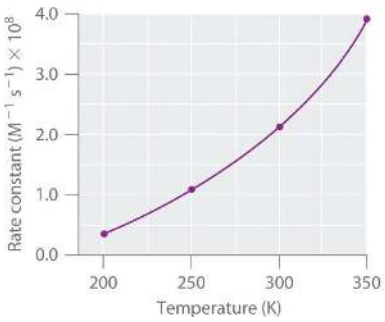


Figure 15.6.1: Rate Constant versus Temperature for the Reaction of NO with O_3The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, 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 15.6.2 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.

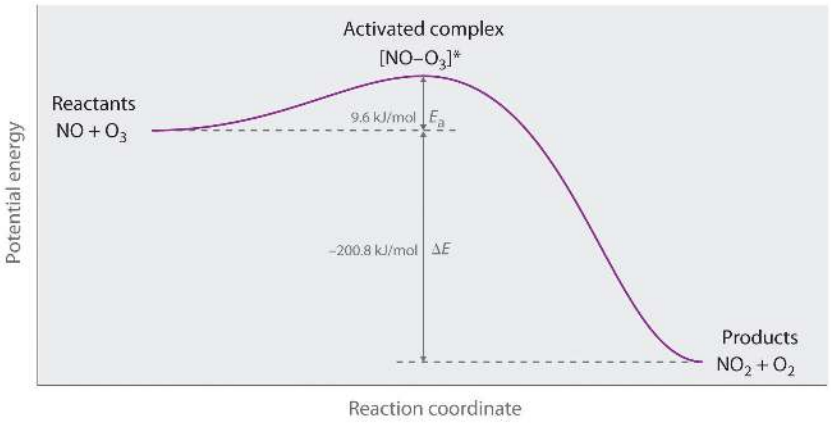


Figure 15.6.2: Energy of the Activated Complex for the NO–O_3 System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex. (CC BY-SA-NC; anonymous)

Figure 15.6.3*a* illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, Figure 15.6.3*b* 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.

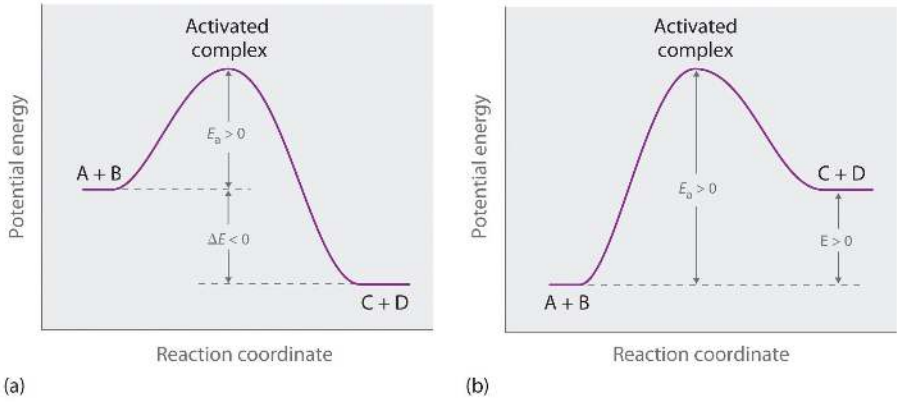


Figure 15.6.3: Differentiating between E_a and ΔE. The potential energy diagrams for a reaction with (a) $\Delta E < 0$ and (b) $\Delta E > 0$ illustrate the change in the potential energy of the system as reactants are converted to products. In both cases, E_a is positive. For a reaction such as the 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 15.6.4 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.

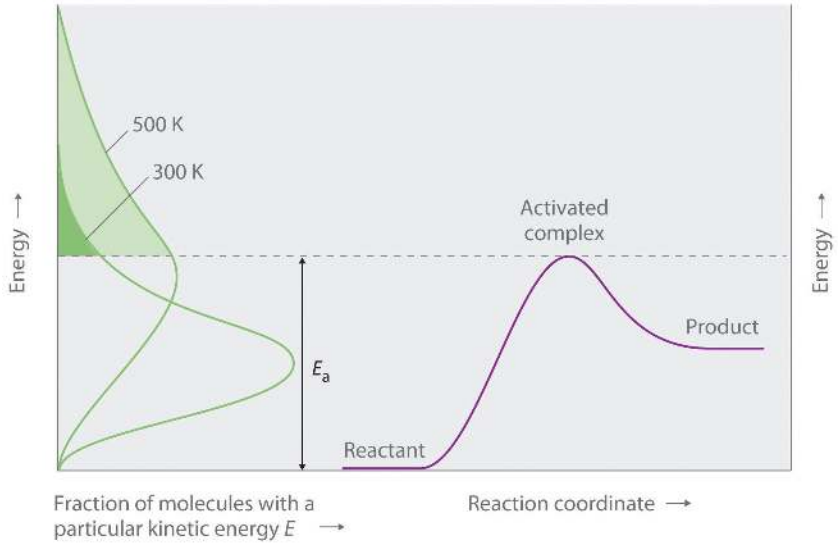
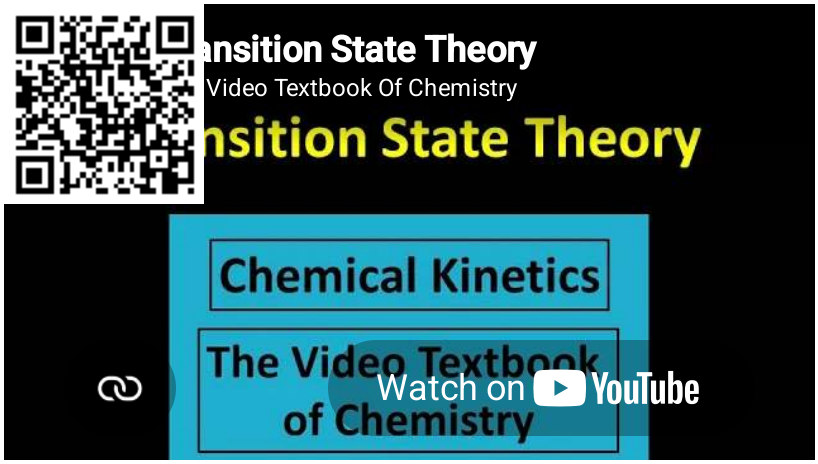


Figure 15.6.4: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution 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.



Video Discussing Transition State Theory: Transition State Theory(opens in new window) [youtu.be]

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 O_3 to produce NO_2 and O_2, a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure 15.6.4). 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).

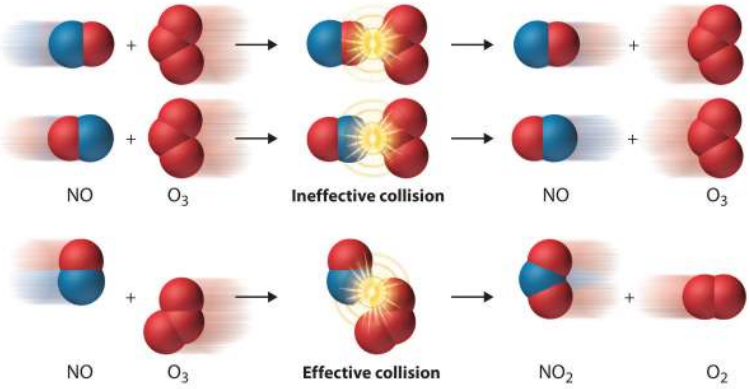


Figure 15.6.4: The Effect of Molecular Orientation on the Reaction of NO and $\mathrm{O_3}$. Most collisions of NO and $\mathrm{O_3}$ molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of $\mathrm{O_3}$ 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

$$\text{rate} = k[A][B] \tag{15.6.2}$$

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**:

$$k = Ae^{-E_a/RT} \tag{15.6.3}$$

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 15.6.1). 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 15.6.3 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 15.6.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) \tag{15.6.4}$$

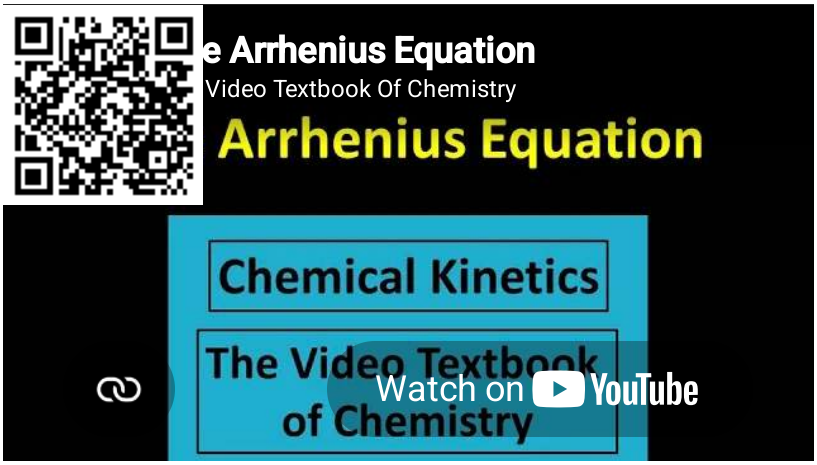
$$= \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \tag{15.6.5}$$

Equation 15.6.5 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 15.6.1.



A Video Discussing The Arrhenius Equation: The Arrhenius Equation(opens in new window) [youtu.be]

Example 15.6.1: 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 15.6.5 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 15.6.6).

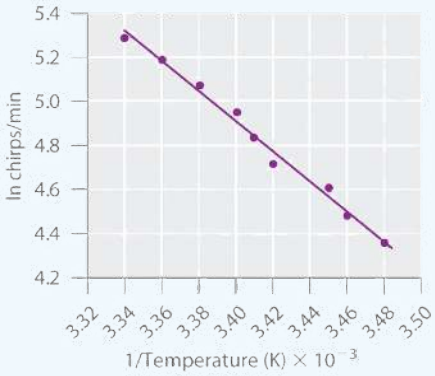


Figure 15.6.6: Graphical Determination of E_a for Tree Cricket Chirping. When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol. (CC 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 15.6.6 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 15.6.5 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - \frac{E_\text{a}}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_\text{a}}{RT_2}$$

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 15.6.1A

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

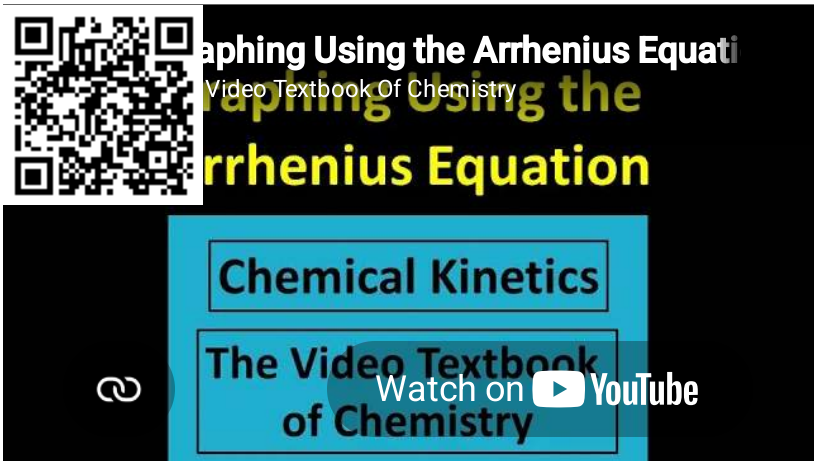
E_a = 114 kJ/mol; k_{700}= 18,600 $M^{-1}\cdot s^{-1}$ = 1.86 × 10^4 $M^{-1}\cdot s^{-1}$.

? Exercise 15.6.1B

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C?

Answer

about 51 kJ/mol



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 $k = Ae^{-Ea/RT}$. 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 $-E_a/R$.

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15.7: 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:

$$2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \longrightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g) \tag{15.7.1}$$

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.

$$NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g) \tag{15.7.2}$$

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:

$$rate = k[NO_2]^2 \tag{15.7.3}$$

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!)

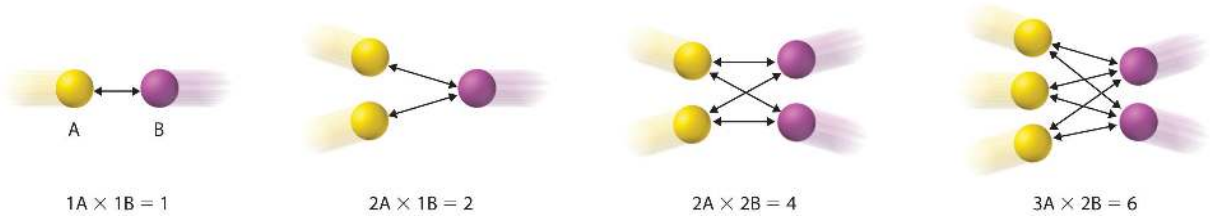


Figure 15.7.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases 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 15.7.1). 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 15.7.1. For a bimolecular elementary reaction of the form A + B → products, the general rate law is

$$rate = k[A][B].$$

Table 15.7.1: 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	$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$	$\text{rate} = k_1[NO_2]^2$ (predicted)
step 2	$\underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}$	$\text{rate} = k_2[NO_3][CO]$ (predicted)
sum	$NO_2 + CO \xrightarrow{k} NO + CO_2$	$\text{rate} = k[NO_2]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

Example 15.7.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of NO_2 with CO with 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 15.7.1

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	$ICl + H_2 \xrightarrow{k_1} HCl + HI$	rate $= k_1[ICl][H_2]$ (slow)
step 2	$\underline{HI + ICl \xrightarrow{k_2} HCl + I_2}$	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 15.7.2 : 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 H_2 occurs via a three-step process

step 1	$NO + NO \xrightarrow{k_1} N_2O_2$	(fast)
step 2	$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$	(slow)
step 3	$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$	(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:

$$\text{rate} = k[NO]^2[H_2]? \qquad \text{(observed)}$$

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

$$2\,\mathrm{NO\,(g)} + 2\,\mathrm{H_2\,(g)} \longrightarrow \mathrm{N_2\,(g)} + 2\,\mathrm{H_2O\,(g)}$$

- 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 $k = k_1k_2$.



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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15.8: 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 15.8.1). 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.

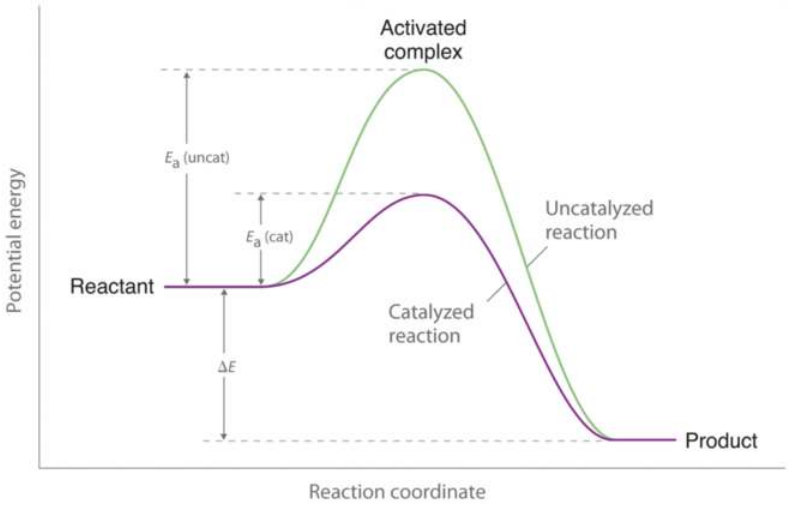


Figure 15.8.1: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect 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 15.8.2, 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.

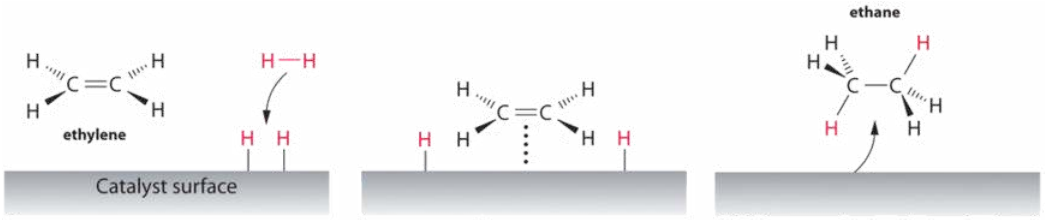


Figure 15.8.2: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 15.8.2 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 15.8.1. 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.

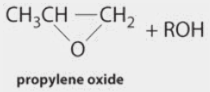
Table 15.8.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

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 15.8.2), 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 15.8.2: 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 15.8.3).



Figure 15.8.3: 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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CHAPTER OVERVIEW

16: Chemical Equilibrium

16.1: Fetal Hemoglobin and Equilibrium

16.2: The Concept of Dynamic Equilibrium

16.3: The Equilibrium Constant (K)

16.4: Expressing the Equilibrium Constant in Terms of Pressure

16.5: Heterogenous Equilibria - Reactions Involving Solids and Liquids

16.6: The Reaction Quotient- Predicting the Direction of Change

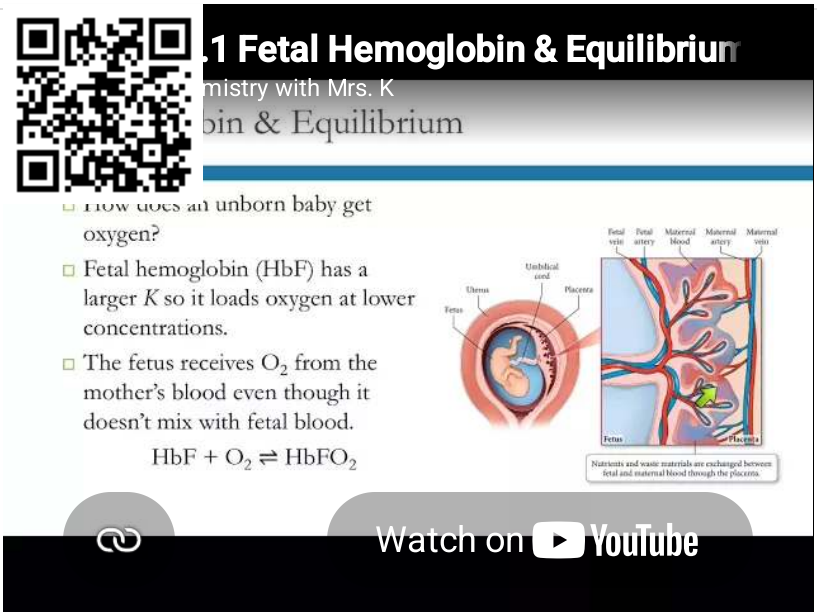
16.7: Finding Equilibrium Concentrations

16.8: Le Châtelier's Principle- How a System at Equilibrium Responds to Disturbances

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16.1: Fetal Hemoglobin and Equilibrium



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16.2: The Concept of 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 16.2.1: 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 (N_2O_4) to nitrogen dioxide (NO_2). You may recall that NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid 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 NO_2 appears (Figure 16.2.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$\underset{colorless}{N_2O_4\,(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{red-brown}{2\,NO_2\,(g)} \tag{16.2.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4\,(g) \xrightarrow{k_f} 2\,NO_2\,(g) \tag{16.2.2}$$

and reverse reaction

$$2\,NO_2\,(g) \xrightarrow{k_r} N_2O_4\,(g) \tag{16.2.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure 16.2.2 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 16.2.2*a*), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 16.2.2*b*). Thus equilibrium can be approached from either direction in a chemical reaction.

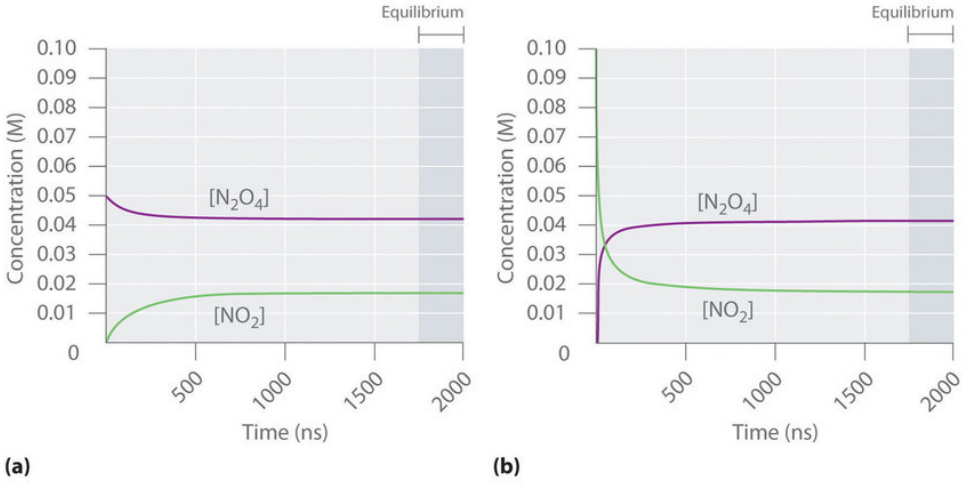


Figure 16.2.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system 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 16.2.3 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 16.2.1 and 16.2.2). 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.

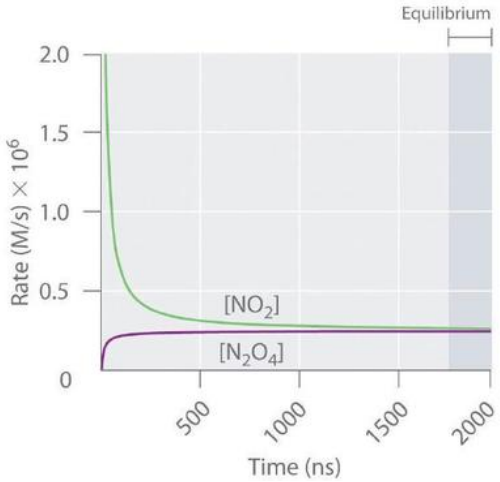


Figure 16.2.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure 16.2.2. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of 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 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 N_2O_4 and NO_2 no longer change.

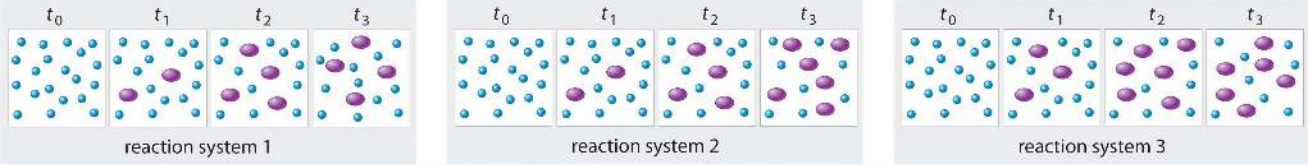
At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

Example 16.2.1

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:

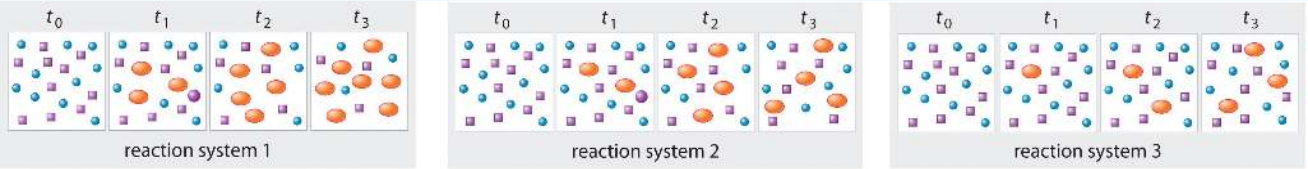
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

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 16.2.1

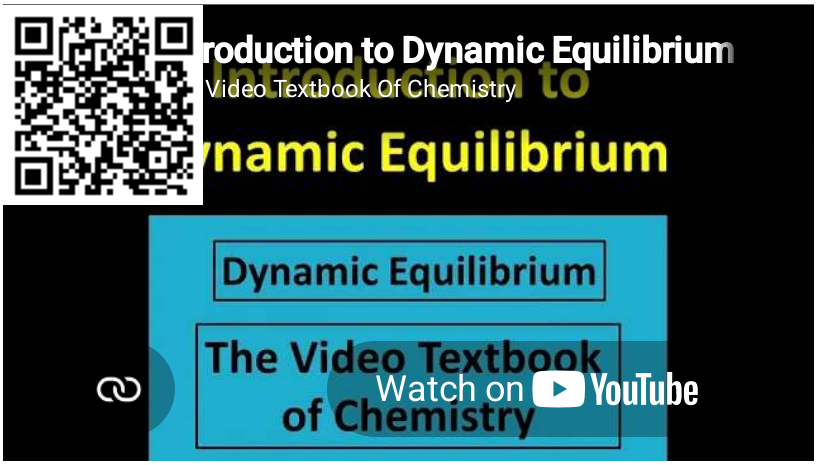
In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



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

system 2



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.

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16.3: The Equilibrium Constant (K)

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of 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:

$$\text{forward rate} = k_f[N_2O_4]$$

and

$$\text{reverse rate} = k_r[NO_2]^2$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{16.3.1}$$

so

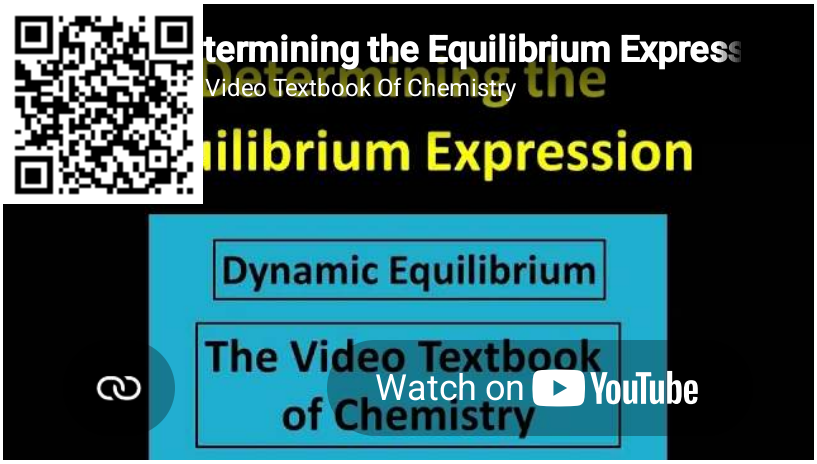
$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{16.3.2}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{16.3.3}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> *The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.*



A Video for Determining the Equilibrium Expression: Determining the Equilibrium Expression(opens in new window) [youtu.be]

Table 16.3.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 16.3.1. 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 ± 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 16.3.1: Initial and Equilibrium Concentrations for NO_2 : N_2O_4 Mixtures at 25°C

[\(\ce{NO2}\)] (M)	Initial Concentrations [\(\ce{NO2}\)] (M)		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{16.3.4}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action (or law of chemical equilibrium) and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{16.3.5}$$

where K is the equilibrium constant for the reaction. Equation 16.3.4 is called the equilibrium equation, and the right side of Equation 16.3.5 is called the equilibrium constant expression. The relationship shown in Equation 16.3.5 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 16.3.2, 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 16.3.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$	300	4.4×10^{53}
$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H2O_{(g)}$	500	2.4×10^{47}
$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$	300	1.6×10^{33}
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	300	4.1×10^{18}
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	300	4.2×10^{13}
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	300	2.7×10^{8}
$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$	100	1.92
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	300	2.9×10^{-1}
$I_{2(g)} \rightleftharpoons 2I_{(g)}$	800	4.6×10^{-7}
$Br_{2(g)} \rightleftharpoons 2Br_{(g)}$	1000	4.0×10^{-7}
$Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$	1000	1.8×10^{-9}
$F_{2(g)} \rightleftharpoons 2F_{(g)}$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

Effective vs. True Concentrations

You will also notice in Table 16.3.2 that equilibrium constants have no units, even though Equation 16.3.5 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 16.3.6, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{16.3.6}$$

Because equilibrium constants are calculated using "effective concentrations" relative to a standard state of 1 M, values of K are unitless.

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$\mathrm{H_2\,(g) + D_2\,(g) \rightleftharpoons 2\,HD\,(g)}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 16.3.3 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants ⇌ products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 16.3.6 and 16.3.5), when $k_f \gg k_r$, K is a **large**

number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

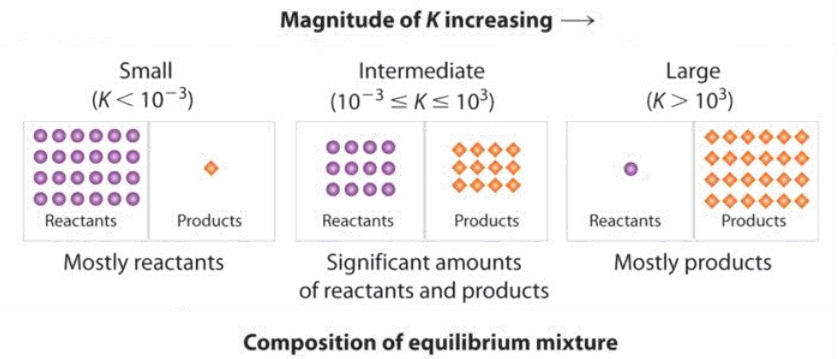


Figure 16.3.3: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

If K is less than 0.001, it is considered small and it will be mostly reactants. If K is greater than 1000, it is considered large and it will be mostly products. If K is greater than or equal to 0.001 and less than or equal to 1000, it is considered intermediate. there will be significant amounts or reactants and products.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

Example 16.3.1: Equilibrium Constant Expressions

Write the equilibrium constant expression for each reaction.

- $\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$
- $\mathrm{CO\,(g) + \frac{1}{2}\,O_2\,(g) \rightleftharpoons CO_2\,(g)}$
- $\mathrm{2\,CO_2\,(g) \rightleftharpoons 2\,CO\,(g) + O_2\,(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 16.3.5. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, $\mathrm{N_2}$ has a coefficient of 1 and $\mathrm{H_2}$ has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and $\mathrm{O_2}$, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[\mathrm{CO_2}]}{[\mathrm{CO}][\mathrm{O_2}]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for $\mathrm{O_2}$. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2

$$\frac{[\mathrm{CO}]^2[\mathrm{O_2}]}{[\mathrm{CO_2}]^2}$$

Exercise 16.3.1

Write the equilibrium constant expression for each reaction.

a. $\mathrm{N_2O\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + \frac{1}{2}\,\mathrm{O_2\,(g)}$
b. $2\,\mathrm{C_8H_{18}\,(g)} + 25\,\mathrm{O_2\,(g)} \rightleftharpoons 16\,\mathrm{CO_2\,(g)} + 18\,\mathrm{H_2O\,(g)}$
c. $\mathrm{H_2\,(g)} + \mathrm{I_2\,(g)} \rightleftharpoons 2\,\mathrm{HI\,(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 16.3.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 16.3.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3\,\mathrm{H_2\,(g)} + \mathrm{N_2\,(g)} \rightleftharpoons 2\,\mathrm{NH_3\,(g)}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,

- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

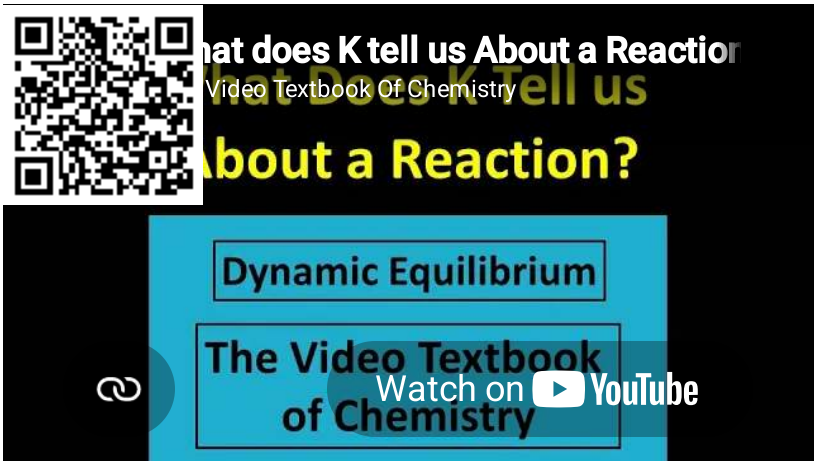
a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C



Video which Discusses What Does K Tell us About a Reaction?: What Does K Tell us About a Reaction?(opens in new window) [youtu.be]

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 16.3.4 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{16.3.7}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{16.3.8}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $\mathrm{N_2O_4} \rightleftharpoons 2\,\mathrm{NO_2}$ is as follows:

$$K = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{16.3.9}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} \tag{16.3.10}$$

Consider another example, the formation of water:

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{H_2O\,(g)}.$$

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

$$2\,NO_2 \rightleftharpoons N_2O_4$$

as

$$NO_2 \rightleftharpoons \tfrac{1}{2}\,N_2O_4$$

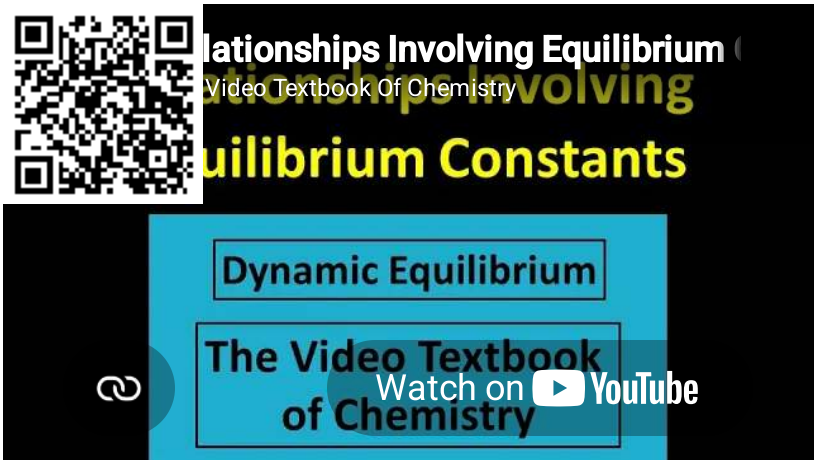
with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{16.3.11}$$

The values for K′ (Equation 16.3.10) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{16.3.12}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the n^{th} power.



A Video Discussing Relationships Involving Equilibrium Constants: Relationships Involving Equilibrium Constants(opens in new window) [youtu.be] (opens in new window)

Example 16.3.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

What is the equilibrium constant for each related reaction at 745 K?

a. $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)$
b. $\tfrac{1}{2}\,N_2\,(g) + \tfrac{3}{2}\,H_2\,(g) \rightleftharpoons NH_3\,(g)$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_{2(g)}$ with $H_{2(g)}$ to produce $NH_{3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

? Exercise

At 527°C, the equilibrium constant for the reaction

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$SO_3\,(g) \rightleftharpoons SO_2\,(g) + \tfrac{1}{2}\,O_2\,(g)$$

Answer

3.6×10^{-3}

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction $aA + bB \rightleftharpoons cC + dD$, in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{16.3.13}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{16.3.14}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The “effective pressure” is called the fugacity, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{16.3.15}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of **gaseous** products and **gaseous** reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 16.3.15, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

\[K_p = K(RT)^1 = KRT \nonumber \]

Example 16.3.4: The Haber Process (again)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 16.3.15 to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation 16.3.12, we have the following:

$$\begin{aligned} K_p &= K(RT)^{-2} \\ &= \frac{K}{(RT)^2} \\ &= \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} \\ &= 3.16 \times 10^{-5} \end{aligned}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 16.3.4

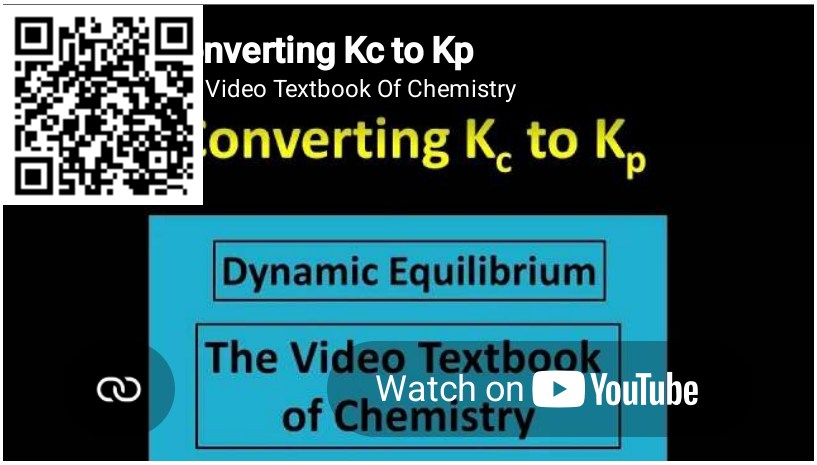
Calculate K_p for the reaction

$$\mathrm{2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$



Video Discussing Converting Kc to Kp: Converting Kc to Kp(opens in new window) [youtu.be]

Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of 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 (step 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 (step 2). The equilibrium constant for each reaction at 100°C is also given.

$$\mathrm{N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)} \qquad K_1 = 2.0 \times 10^{-25}$$

$$\mathrm{2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)} \quad K_2 = 6.4 \times 10^{9}$$

Summing reactions (step 1) and (step 2) gives the overall reaction of N_2 with O_2:

$$\mathrm{N_2\,(g) + 2\,O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)} \qquad K_3 = ?$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

> *To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.*

Example 16.3.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^{4}) = 3.03 \times 10^{3}$$

Exercise 16.3.6

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
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

$K_3 = 1.1 \times 10^{66}$

Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas

during the reaction. An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

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16.4: Expressing the Equilibrium Constant in Terms of Pressure

Learning Objectives

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as CaF_2(s), the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2\,(g) + C\,(s)} \rightleftharpoons \mathrm{2\,CO\,(g)} \tag{16.4.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{\mathrm{CO}}^2}{a_{\mathrm{CO_2}} a_C} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}][1]} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}]} \tag{16.4.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{16.4.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and $\mathrm{CO_2}$, the system described in Equation 16.4.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 16.4.1, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

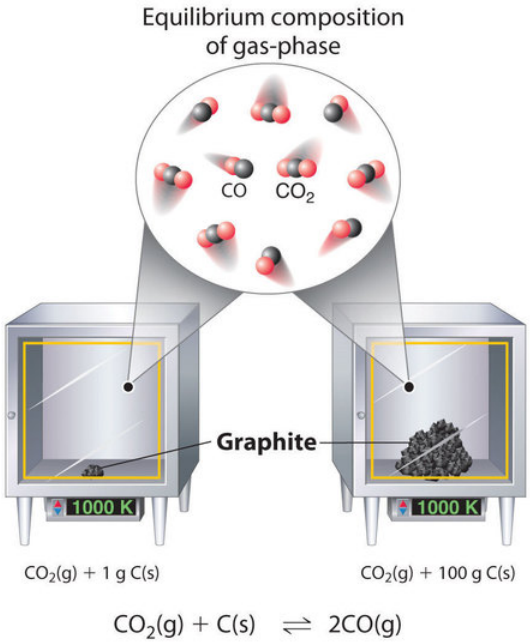


Figure 16.4.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 16.4.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $\mathrm{PCl_3\,(l) + Cl_2\,(g) \rightleftharpoons PCl_5\,(s)}$
b. $\mathrm{Fe_3O_4\,(s) + 4\,H_2\,(g) \rightleftharpoons 3\,Fe\,(s) + 4\,H_2O\,(g)}$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

Exercise 16.4.1

Write the expressions for K and K_p for the following reactions.

a. $\mathrm{CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)}$

b. $\underset{glucose}{\mathrm{C_6H_{12}O_6\,(s)}} + \mathrm{6\,O_2\,(g) \rightleftharpoons 6\,CO_2\,(g) + 6\,H_2O\,(g)}$

Answer a

$K = [\mathrm{CO_2}]$ and $K_p = P_{\mathrm{CO_2}}$

Answer 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 solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

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16.5: Heterogenous Equilibria - Reactions Involving Solids and Liquids

Learning Objectives

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as CaF_2(s), the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2\,(g) + C\,(s)} \rightleftharpoons \mathrm{2\,CO\,(g)} \tag{16.5.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{\mathrm{CO}}^2}{a_{\mathrm{CO_2}} a_C} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}][1]} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}]} \tag{16.5.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{16.5.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and $\mathrm{CO_2}$, the system described in Equation 16.5.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 16.5.1, 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.

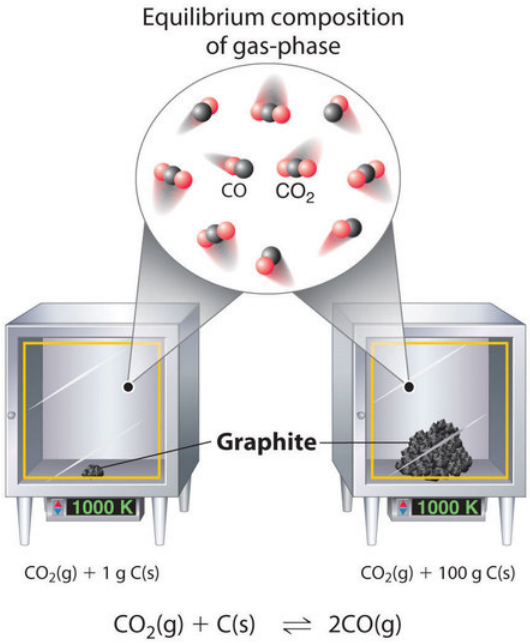


Figure 16.5.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 16.5.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $\mathrm{PCl_3\,(l) + Cl_2\,(g) \rightleftharpoons PCl_5\,(s)}$
b. $\mathrm{Fe_3O_4\,(s) + 4\,H_2\,(g) \rightleftharpoons 3\,Fe\,(s) + 4\,H_2O\,(g)}$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

Exercise 16.5.1

Write the expressions for K and K_p for the following reactions.

a. $\mathrm{CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)}$

b. $\underset{glucose}{\mathrm{C_6H_{12}O_6\,(s)}} + \mathrm{6\,O_2\,(g) \rightleftharpoons 6\,CO_2\,(g) + 6\,H_2O\,(g)}$

Answer a

$K = [\mathrm{CO_2}]$ and $K_p = P_{\mathrm{CO_2}}$

Answer 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 solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

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16.6: The Reaction Quotient- Predicting the Direction of 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:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{16.6.1}$$

To understand how information is obtained using a reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons 2\,\mathrm{NO_2\,(g)}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{16.6.2}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table 16.6.1: Equilibrium Experiment data

Experiment	$[\mathrm{NO_2}]\ (M)$	$[\mathrm{N_2O_4}]\ (M)$	$Q = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K:

- If $Q = K$, for example, then the system is already at equilibrium, and **no further change** in the composition of the system will occur unless the conditions are changed.
- If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the **right** as written, forming products at the expense of reactants.
- If $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the **left** as written, forming reactants at the expense of products.

These points are illustrated graphically in Figure 16.6.1.

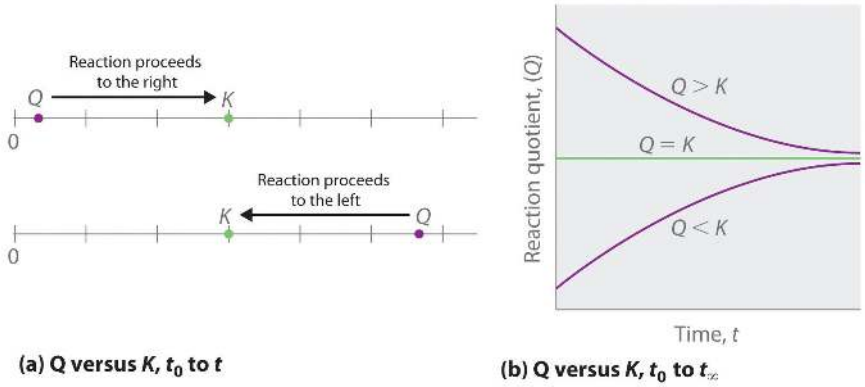
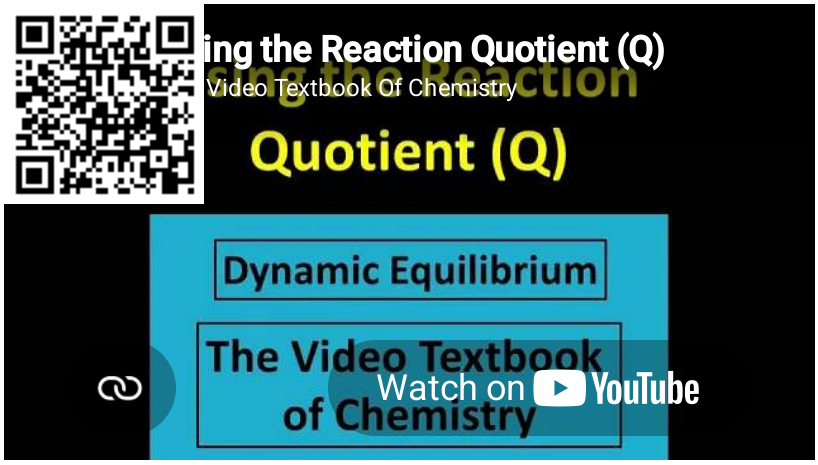


Figure 16.6.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

One way is used two number lines. The second way is to use a graph of reaction quotient against time.

> *If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.*



A Video Discussing Using the Reaction Quotient (Q): Using the Reaction Quotient (Q) (opens in new window) [youtu.be]

Example 16.6.1

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$\mathrm{CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3\,H_2\,(g)}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of

H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and 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 16.6.1 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} mol$ of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2}\,\text{mol}}{2.0\,\text{L}} = 6.0 \times 10^{-3} M$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B We now compute Q and compare it with K:

$$\begin{aligned} Q &= \frac{[CO][H_2]^3}{[CH_4][H_2O]} \\ &= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} \\ &= 9.0 \times 10^{-6} \end{aligned}$$

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 H_2 and CO at the expense of H_2O and CH_4.

? Exercise 16.6.2

In the water–gas shift reaction introduced in Example 16.6.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of 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

$Q = 0.96$. Since (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

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:

$$\mathrm{PbCO_3\,(s) \rightleftharpoons PbO\,(s) + CO_2\,(g)} \tag{16.6.3}$$

Because $\mathrm{PbCO_3}$ and PbO are solids, the equilibrium constant is simply

$$K = [\mathrm{CO_2}].$$

At a given temperature, therefore, any system that contains solid $\mathrm{PbCO_3}$ and solid PbO will have exactly the same concentration of $\mathrm{CO_2}$ at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 16.6.3, which shows a plot of $[\mathrm{CO_2}]$ versus the amount of $\mathrm{PbCO_3}$ added. Initially, the added $\mathrm{PbCO_3}$ decomposes completely to $\mathrm{CO_2}$ because the amount of $\mathrm{PbCO_3}$ is not sufficient to give a $\mathrm{CO_2}$ concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only $\mathrm{CO_2\,(g)}$ and $\mathrm{PbO\,(s)}$. In contrast, when just enough $\mathrm{PbCO_3}$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $\mathrm{PbCO_3}$ has no effect on the $\mathrm{CO_2}$ concentration: the graph is a horizontal line.

Thus any $\mathrm{CO_2}$ concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $\mathrm{PbCO_3}$ and PbO are present. For example, the point labeled **A** in Figure 16.6.2 lies above the horizontal line, so it corresponds to a $[\mathrm{CO_2}]$ that is greater than the equilibrium concentration of $\mathrm{CO_2}$ (i.e., $Q > K$). To reach equilibrium, the system must decrease $[\mathrm{CO_2}]$, which it can do only by reacting $\mathrm{CO_2}$ with solid PbO to form solid $\mathrm{PbCO_3}$. Thus the reaction in Equation 16.6.3 will proceed to the left as written, until $[\mathrm{CO_2}] = K$. Conversely, the point labeled **B** in Figure 16.6.2 lies below the horizontal line, so it corresponds to a $[\mathrm{CO_2}]$ that is less than the equilibrium concentration of $\mathrm{CO_2}$ (i.e., $Q < K$). To reach equilibrium, the system must increase $[\mathrm{CO_2}]$, which it can do only by decomposing solid $\mathrm{PbCO_3}$ to form $\mathrm{CO_2}$ and solid PbO. The reaction in Equation 16.6.3 will therefore proceed to the right as written, until $[\mathrm{CO_2}] = K$.

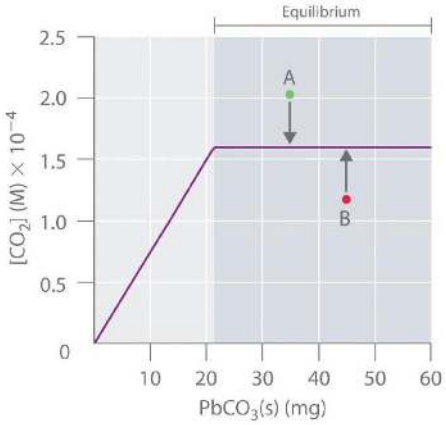


Figure 16.6.2: The Concentration of Gaseous $\mathrm{CO_2}$ in a Closed System at Equilibrium as a Function of the Amount of Solid $\mathrm{PbCO_3}$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $\mathrm{PbCO_3}$ added, as $\mathrm{PbCO_3}$ decomposes to $\mathrm{CO_2\,(g)}$ and solid PbO. Once the $\mathrm{CO_2}$ concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $\mathrm{PbCO_3}$ has no effect on $[\mathrm{CO_2}]$, as long as the temperature remains constant.

Reaction 2

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$\mathrm{CdO\,(s) + H_2\,(g) \rightleftharpoons Cd\,(s) + H_2O\,(g)} \tag{16.6.4}$$

and the equilibrium constant is

$$K = \frac{[\mathrm{H_2O}]}{[\mathrm{H_2}]}.$$

If $[\mathrm{H_2O}]$ is doubled at equilibrium, then $[\mathrm{H_2}]$ must also be doubled for the system to remain at equilibrium. A plot of $[\mathrm{H_2O}]$ versus $[\mathrm{H_2}]$ at equilibrium is a straight line with a slope of K (Figure 16.6.3). Again, only those pairs of concentrations of $\mathrm{H_2O}$ and $\mathrm{H_2}$ that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line

corresponds to a nonequilibrium state. In such cases, the reaction in Equation 16.6.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point **A** in Figure 16.6.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (i.e., $Q < K$). Thus the reaction in Equation 16.6.4 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point **B** in Figure 16.6.3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 16.6.4 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

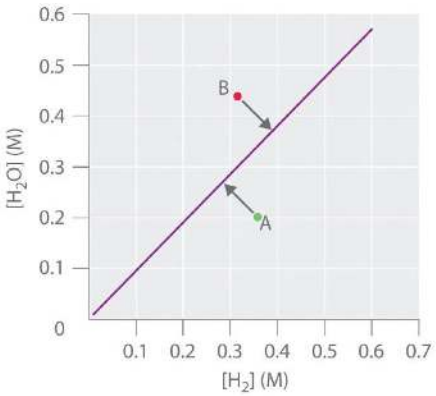


Figure 16.6.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of $H_{2(g)}$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

Reaction 3

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I\,(s) \rightleftharpoons NH_3\,(g) + HI\,(g) \tag{16.6.5}$$

For this system, K is equal to the product of the concentrations of the two products:

$$K = [NH_3][HI].$$

If we double the concentration of NH_3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 16.6.4. As a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which

$$[NH_3] = [HI] = \sqrt{K}.$$

Any point that lies below and to the left of the equilibrium curve (such as point **A** in Figure 16.6.4) corresponds to $Q < K$, and the reaction in Equation 16.6.5 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point **B** in Figure 16.6.5) corresponds to $Q > K$, and the reaction in Equation 16.6.5 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

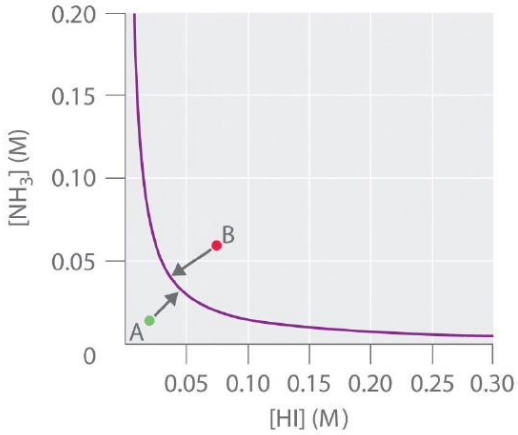


Figure 16.6.4: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for system in Reaction 16.6.5 at Equilibrium. Only one equilibrium concentration of $NH_3\,(g)$ is possible for any given equilibrium concentration of $HI\,(g)$. In this case, the two are inversely proportional. Thus a large [HI] at equilibrium requires a small $[NH_3]$ 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.

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16.7: Finding Equilibrium Concentrations

Learning Objectives

- To solve quantitative problems involving chemical equilibriums.

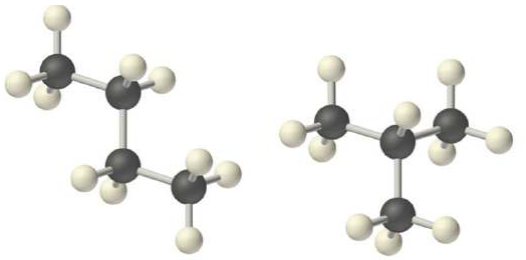
There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 that the equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$n\text{-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{16.7.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{16.7.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 16.7.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we use the relationship derived previously

$$K_p = K(RT)^{\Delta n}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

Exercise 16.7.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$2NOCl_{(g)} \leftrightharpoons 2NO_{(g)} + Cl_{2(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer

$K = 48.8$ and $K_p = 48.8$

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 16.7.2 shows one way to do this.

Example 16.7.2

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:

\[2 NOCl_{(g)} \rightleftharpoons 2NO_{(g)}+Cl_{2(g)}\nonumber \]

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).

B. Calculate all possible initial concentrations from the data given and insert them in the table.

C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.

D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$. The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$. We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([NOCl]	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

? Exercise 16.7.2

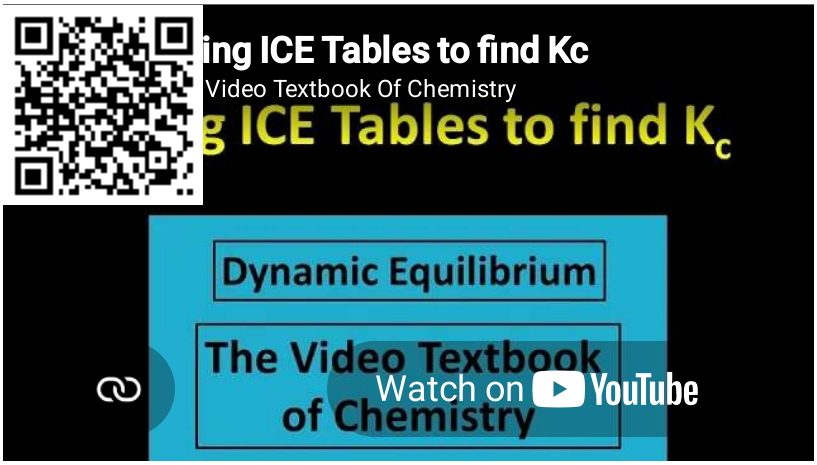
The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer

$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$



A Video Disucssing Using ICE Tables to find Kc: Using ICE Tables to find Kc(opens in new window) [youtu.be]

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 16.7.1), 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 16.7.2.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of n-butane is Δ[n-butane] = $-x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
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,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for x,

$$x = 2.6(1.00 - x) = 2.6 - 2.6x$$

$$x + 2.6x = 2.6$$

$$x = 0.72$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6$$

This is the same K we were given, so we can be confident of our results.

Example 16.7.3 illustrates a common type of equilibrium problem that you are likely to encounter.

Example 16.7.3: The water–gas shift reaction

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.0150 - x)$	$(0.0150 - x)$	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150 - x)(0.0150 - x} = \frac{x^2}{(0.0150 - x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150 - x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150 - x)} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

? Exercise 16.7.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

- $[HI]_f = 0.270\ M$
- $[H_2]_f = [I_2]_f = 0.037\ M$

In Example 16.7.3, 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 16.7.4.

Example 16.7.4

In the water–gas shift reaction shown in Example 16.7.3, a sample containing 0.632 M CO2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (\(x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.570 - x)$	$(0.632 - x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 16.7.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[=[H_2]_i+\Delta[H_2]=0.570\ M-0.148\ M=0.422M$
- $[CO_2]_f=[CO_2]_i+\Delta[CO_2]=0.632\ M-0.148\ M=0.484M$
- $[H_2O]_f=[H_2O]_i+\Delta[H_2O]=0\ M+0.148\ M=0.148\ M$
- $[CO]_f=[CO]_i+\Delta[CO]=0M+0.148\ M=0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(0.148)^2}{(0.422)(0.484)}=0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

? Exercise 16.7.4

The exercise in Example 16.7.1 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

- $[H_I]_f=0.0882\ M$
- $[H_2]_f=0.156\ M$
- $[I_2]_f=9.2\times10^{-4}M$

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 ($K\leq10^{-3}$) or very large ($K\geq10^3$), 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 16.7.5.

✔ Example 16.7.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)}+O_{2(g)}\rightleftharpoons2NO_{(g)}$$

with $K_p=2.0\times10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P_{N_2}=0.78\ atm$ and $P_{O_2}=0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (\(x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO

produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	$-x$	$-x$	$+2x$
Final	$(0.78-x)$	$(0.21-x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78-x)(0.21-x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78-x) = 0.78$ and $(0.21-x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x = 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78-x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21-x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^3$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? Exercise 16.7.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer

$4.8 \times 10^{-31}\ atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 16.7.6.

Example 16.7.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

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 16.7.5. 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,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified ($(0.045 + x)$ = 0.045 and $(0.155 - x) = 0.155$) as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

? Exercise 16.7.6

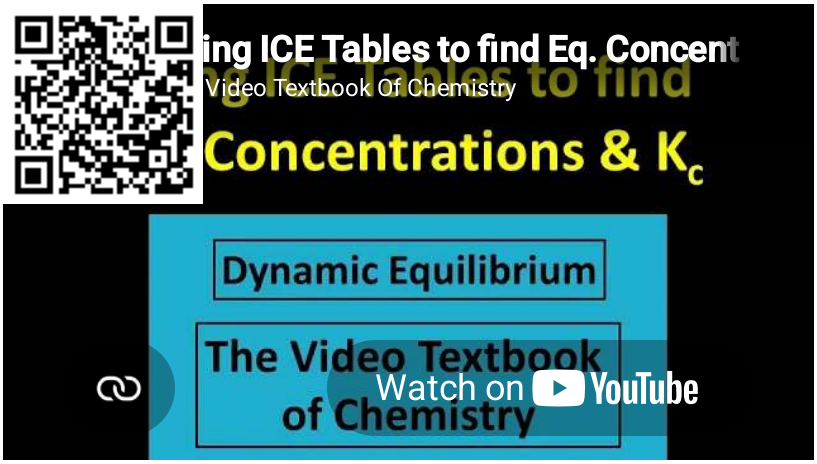
Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ M\ [Cl_2]_f = 0.135\ M\ [HCl]_f = 0.514\ M$



A Video Discussing Using ICE Tables to find Eq. Concentrations & Kc: Using ICE Tables to find Eq. Concentrations & Kc(opens in new window) [youtu.be]

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture. When an equilibrium constant is calculated

from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

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16.8: Le Châtelier's Principle- How a System at Equilibrium Responds to Disturbances

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 16.8.1 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 16.8.1: (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:

$$\mathrm{H_2\,(g) + I_2\,(g)} \rightleftharpoons \mathrm{2\,HI\,(g)} \tag{16.8.1}$$

$$K_c = 50.0 \text{ at } 400^\circ\mathrm{C} \tag{16.8.2}$$

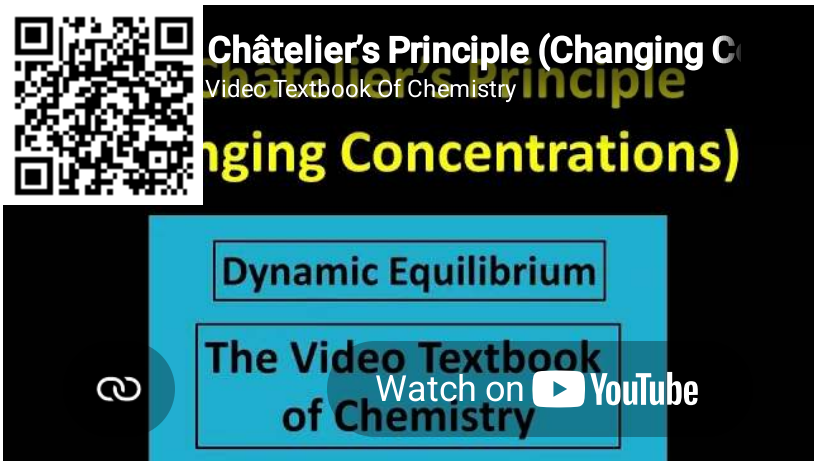
The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[\mathrm{H_2}] = [\mathrm{I_2}] = 0.221\ M$ and $[\mathrm{HI}] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If $\mathrm{H_2}$ is introduced into the system so quickly that its concentration doubles before it begins to react (new $[\mathrm{H_2}] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[\mathrm{H_2}] = 0.374\ M$,
- $[\mathrm{I_2}] = 0.153\ M$, and
- $[\mathrm{HI}] = 1.692\ M$.

This gives:

$$\begin{aligned} Q_c &= \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} \\ &= \frac{(1.692)^2}{(0.374)(0.153)} \\ &= 50.0 = K_c \end{aligned}$$

We have stressed this system by introducing additional $\mathrm{H_2}$. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess $\mathrm{H_2}$, reducing the amount of uncombined $\mathrm{I_2}$, and forming additional HI. **Le Chatelier's Principle (Changing Concentrations):** Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be]



A Video Discussing Le Chatelier's Principle (Changing Concentrations): Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be] (opens in new window)

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

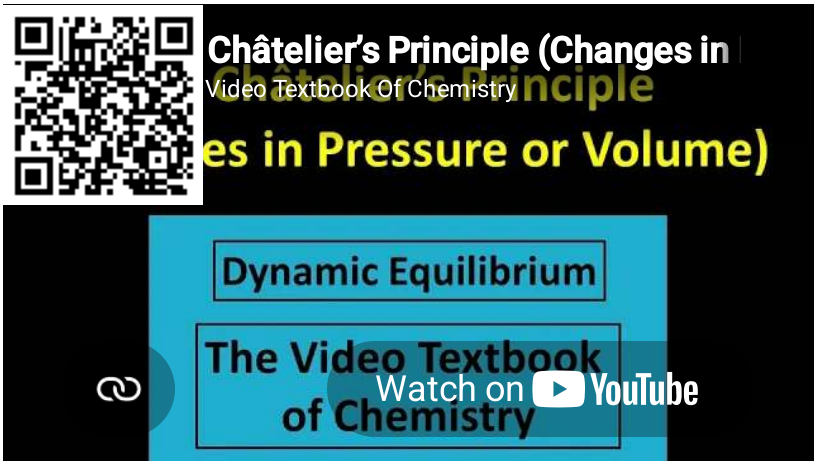
$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \tag{16.8.3}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and 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 NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) \tag{16.8.4}$$

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.



Le Chatelier's Principle (Changes in Pressure or Volume):

Le Chatelier's Principle (Changes in Pressure or Volume)(opens in new window) [youtu.be]

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \quad \Delta H = -9.4\ \text{kJ (exothermic)} \tag{16.8.5}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) + \text{heat} \tag{16.8.6}$$

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 NO_2 and N_2O_4 in this reaction

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons \mathrm{2\,NO_2\,(g)} \quad \Delta H = 57.20\ \mathrm{kJ} \tag{16.8.7}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathrm{heat + N_2O_4\,(g)} \rightleftharpoons \mathrm{2\,NO_2\,(g)} \tag{16.8.8}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown 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 N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

The overview of how different disturbances affect the reaction equilibrium properties is tabulated in Table 16.8.1.

Table 16.8.1: 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
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Example 16.8.1

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 16.8.1

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

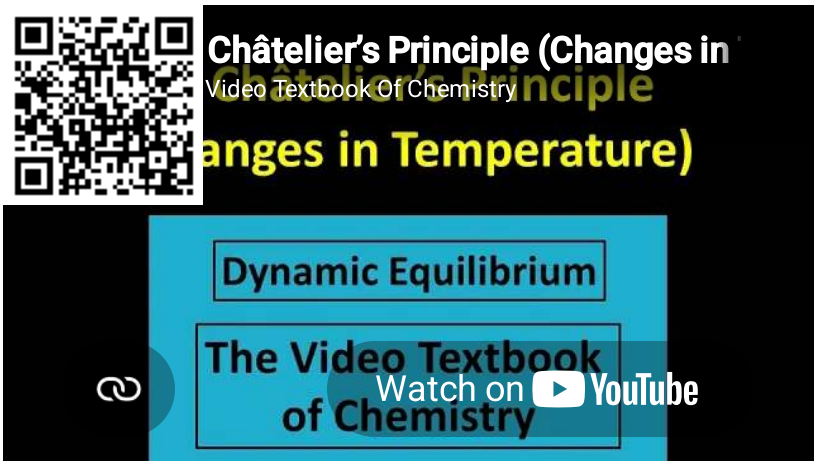
$K = \frac{[H_2]}{[HBr]}$; $[H_2]$ must decrease by about a factor of 3.

Answer b

$K = \frac{1}{[N_2]}$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.

Answer c

$K = \frac{1}{[SO_2][Cl_2]}$; $[SO_2]$ must decrease by about half.



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

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)} \tag{16.8.9}$$

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 16.8.9). 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 16.8.1: 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

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CHAPTER OVERVIEW

17: Acids and Bases

17.1: Batman’s Basic Blunder
17.2: The Nature of Acids and Bases
17.3: Definitions of Acids and Bases
17.4: Acid Strength and Molecular Structure
17.5: Acid Strength and the Acid Ionization Constant (Ka)
17.6: Autoionization of Water and pH
17.7: Finding the [H3O+] and pH of Strong and Weak Acid Solutions
17.8: Finding the [OH-] and pH of Strong and Weak Base Solutions
17.9: The Acid-Base Properties of Ions and Salts
17.10: Polyprotic Acids
17.11: Lewis Acids and Bases

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17.1: Batman’s Basic Blunder



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17.2: The Nature of Acids and Bases

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 17.2.1).

Table 17.2.1: 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.

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17.3: Definitions 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

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Previously, we defined acids and bases as Arrhenius did: An acid is a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ${}^1_1H$, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{17.3.1}$$

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):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{17.3.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{17.3.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{17.3.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{17.3.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{17.3.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{17.3.7}$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{17.3.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{17.3.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{17.3.10}$$

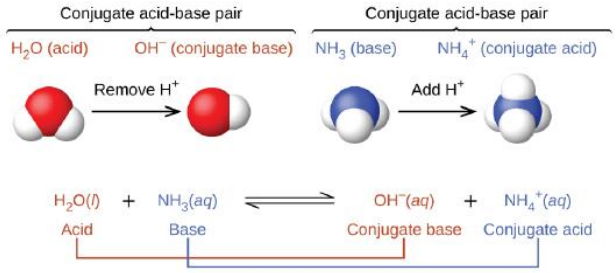
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{17.3.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{17.3.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{17.3.13}$$

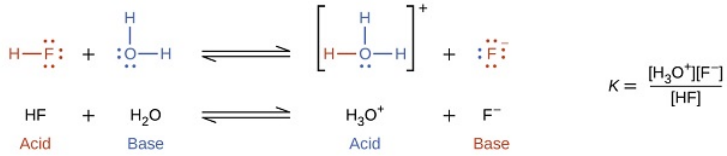
\[\ce{F^- +H^+ \rightleftharpoons HF} \label{16.2.3g} \]

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



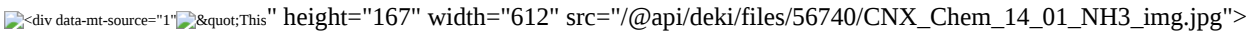
A conjugate acid base pair if when we remove a H plus from the acid to get the conjugate base. Another conjugate acid base pair is when we add H plus to a base to get a conjugate acid. In a reaction: the acid and base are the reactants and the products are the conjugate base and conjugate acid.

The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:

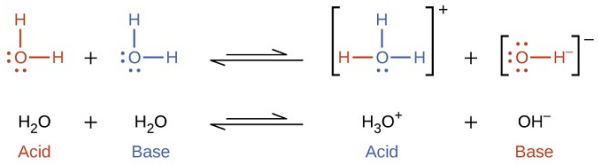


In this reaction HF is treated as the acid and water is treated as the base. The products as H3O plus and F minus. H3O plus is the acid and F minus is the base.

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:

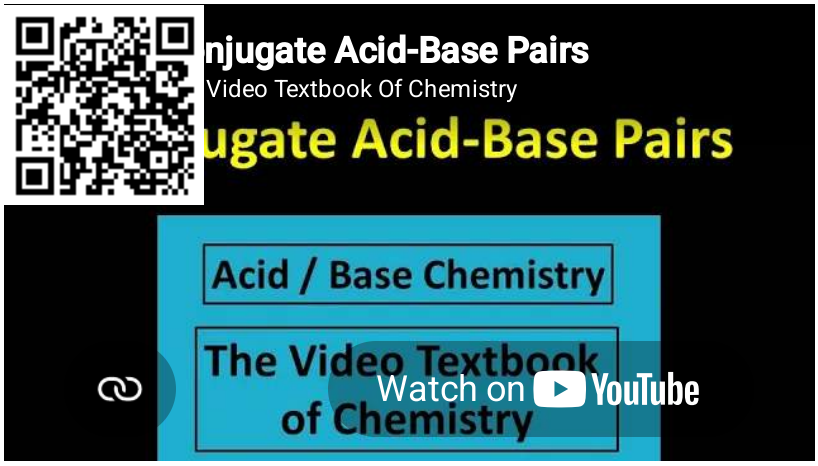


Here we have 2 water molecules reacting together. One water molecule is an acid while the second water molecule acts as a base. For the products, we get H3O plus and OH minus. H3O plus is the acid and OH minus is the base.

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + HO^-{}_{(aq)} \quad K_w = [H_3O^+][OH^-] \tag{17.3.14}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.



A Video Discussing Conjugate Acid-Base Pairs: Conjugate Acid-Base Pairs [youtu.be]

Example 17.3.1: 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, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^{2+} = [OH^-]^{2+} = 1.0 \times 10^{-14}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

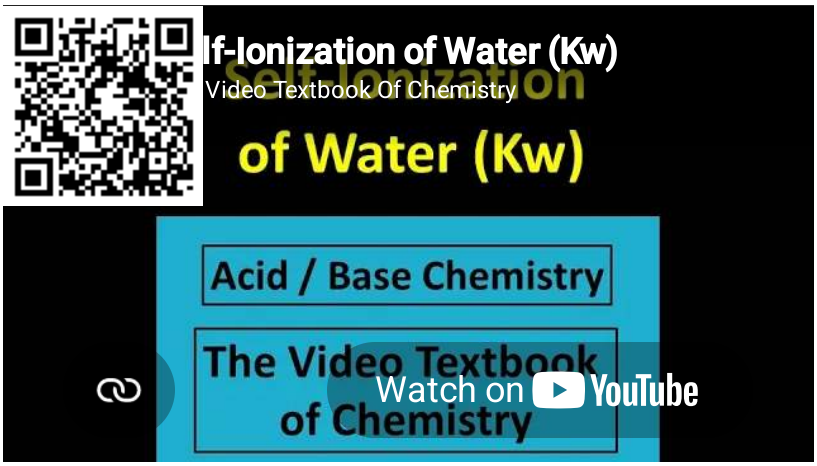
Exercise 17.3.1

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

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium determined by the autoionization reaction but it does shift the relative concentrations of $[OH^-]$ and $[H_3O^+]$. Example 16.2.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.



A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw) [youtu.be]

Example 17.3.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 17.3.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$\mathrm{HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}_{3(aq)} + H_3O^+_{(aq)}} \tag{17.3.15}$$

$$\mathrm{HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-_{(aq)}} \tag{17.3.16}$$

Example 17.3.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $HSO^-_{3(aq)} + OH^-_{(aq)} \rightleftharpoons SO^{2-}_{3(aq)} + H_2O_{(l)}$
b. $HSO^-_{3(aq)} + HI_{(aq)} \rightleftharpoons H_2SO_{3(aq)} + I^-_{(aq)}$

Example 17.3.4

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer

a. $H_2PO^-_{4(aq)} + HBr_{(aq)} \rightleftharpoons H_3PO_{4(aq)} + Br^-_{(aq)}$
b. $H_2PO^-_{4(aq)} + OH^-_{(aq)} \rightleftharpoons HPO^{2-}_{4(aq)} + H_2O_{(l)}$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, $\mathrm{H_3O^+}$, and the hydroxide ion, $\mathrm{OH^-}$ when it undergoes autoionization:

$$\mathrm{2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_\mathrm{w} = [\mathrm{H_2O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 25°\mathrm{C}$$

Key Equations

- $$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}\,] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

Glossary

acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization
reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

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17.4: Acid Strength and Molecular Structure

Learning Objectives

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the $\mathrm{A–H}$ or $\mathrm{B–H^+}$ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{17.4.1}$$

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:

$$CH_4(\ 50) \ll NH_3(\ 36) < H_2O(14.00) < HF(3.20) \tag{17.4.2}$$

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.

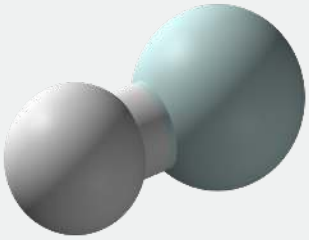
The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate 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).

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 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:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{17.4.3}$$

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 17.4.1, 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 17.4.1 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 17.4.1 and Figure 17.4.2, 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.

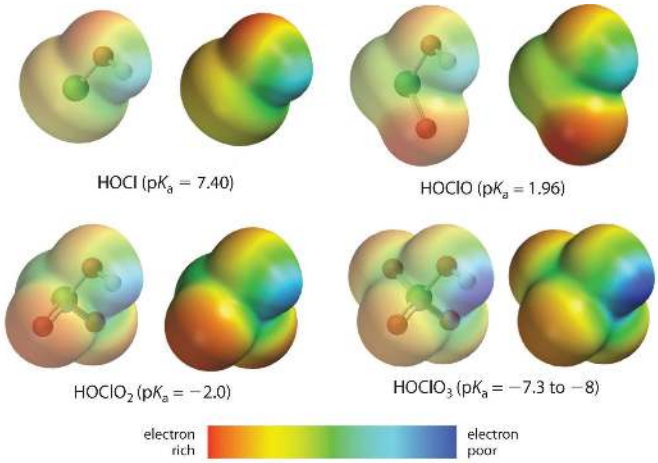
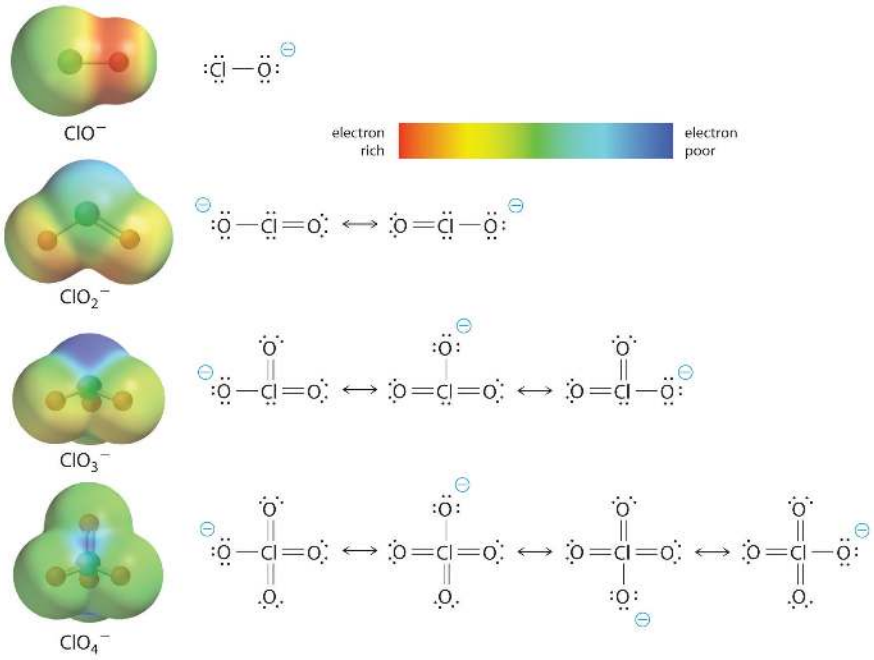


Figure 17.4.1: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron 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 17.4.2, 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.

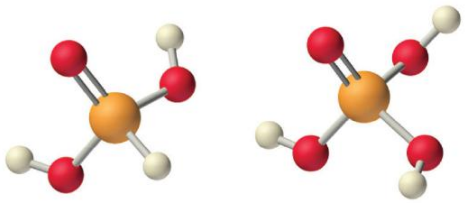
> *Electron delocalization in the conjugate base increases acid strength.*

The electrostatic potential plots in Figure 17.4.2 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 17.4.2). 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 O–H bond and increasing the strength of the oxoacid.



Careful inspection of the data in Table 17.4.1 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 17.4.1: 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:

$$pK_a CH_3CO_2H 4.76 < CH_2ClCO_2H 2.87 < CHCl_2CO_2H 1.35 < CCl_3CO_2H 0.66 < CF_3CO_2H 0.52$$

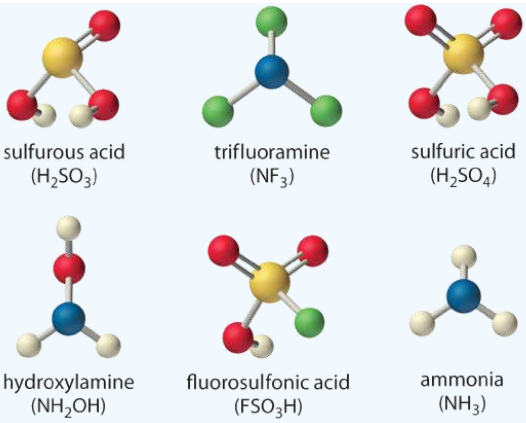
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-CH_3$ group of acetic acid by a $-CF_3$ group results in about a 10,000-fold increase in acidity!

Example 17.4.1

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:

$$pKaH_2SO_31.85 < H_2SO_4^{-2} < FSO_3H - 10$$

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:

$$pK_bNF_3— << NH_2OH8.06 < NH_34.75$$

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 17.4.1

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

$HClO-3 > CH_3PO_3H_2 > H_3PO_4$

Answer a

$CF_3S^- < CH_3S^- < OH^-$

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 O−H bond and allow hydrogen to be more easily lost as H^+ ions.

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17.5: Acid Strength and the Acid Ionization Constant (Ka)

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:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{17.5.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{17.5.2}$$

As we noted earlier, because water is the solvent, it has an activity equal to 1, so the $[H_2O]$ term in Equation 17.5.2 is actually the a_{H_2O}, which is equal to 1.

Again, for simplicity, H_3O^+ can be written as H^+ in Equation 17.5.3.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \tag{17.5.3}$$

Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form hydronium ions, H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them unitless. The values of K_a for a number of common acids are given in Table 17.5.1.

Table 17.5.1: 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
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{17.5.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{17.5.5}$$

Once again, the activity of water has a value of 1, so water does not appear in the equilibrium constant expression. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 17.5.2.

Table 17.5.2: 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 17.5.1.

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:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{17.5.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{17.5.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{17.5.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{17.5.9}$$

If we add Equations 17.5.6 and 17.5.7, we obtain the following:

add Equations 17.5.6 and 17.5.7, we obtain

Reaction	Equilibrium Constants
$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}}$	$K_a = [H^+]\,\cancel{[CN^-]} \,/\, \cancel{[HCN]}$
$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}}$	$K_b = [OH^-]\,\cancel{[HCN]} \,/\, \cancel{[CN^-]}$
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	$K = K_a \times K_b = [H^+][OH^-]$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{17.5.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{17.5.11}$$

$$K_a = 10^{-pK_a} \tag{17.5.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{17.5.13}$$

$$K_b = 10^{-pK_b} \tag{17.5.14}$$

Similarly, Equation 17.5.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{17.5.15}$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \tag{17.5.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Tables 17.5.1 and 17.5.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

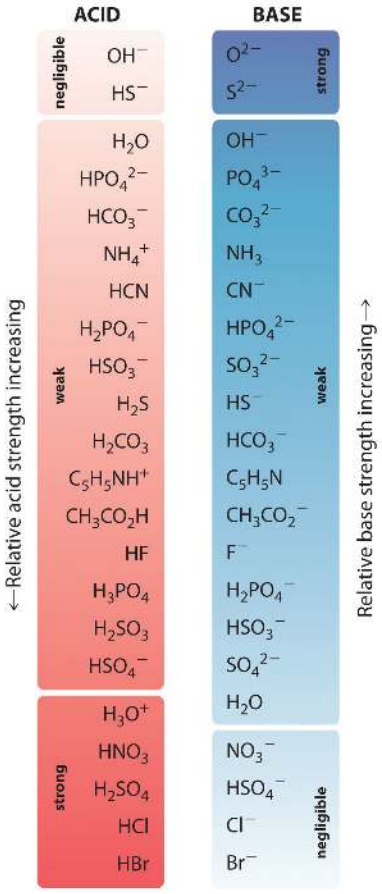


Figure 17.5.1: The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Strong acids are H3O plus, HNO3, H2SO4, HCl, and HBr. Negligible acids are HS minus and OH minus. Stron bases are O negative 2, S negative 2. Negligible bases are NO3 minus, HSO4 minus, Cl minus, and Br minus.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 17.5.1. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This

order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 17.5.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

> *The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{17.5.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_{2(aq)}{}^-}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

> *All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

Example 17.5.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.

b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 17.5.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equations 17.5.15 and 17.5.16. Use the relationships pK = −log K and K = 10^{-pK} (Equations 17.5.11 and 17.5.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 17.5.16: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 17.5.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

? Exercise 17.5.1: 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

- $K_a = 1.4 \times 10^{-4}$ for lactic acid;
- pK_b = 10.14 and
- $K_b = 7.2 \times 10^{-11}$ for the lactate ion



A Video Calculating pH in Strong Acid or Strong Base Solutions: Calculating pH in Strong Acid or Strong Base Solutions [youtu.be]

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 17.5.1 that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which

means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I− or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table 17.5.1 were determined using measurements like this and different nonaqueous solvents.

> *In aqueous solutions, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.*

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH− is leveled to the strength of OH− because OH− is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 17.5.2, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{17.5.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{17.5.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{17.5.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

As you learned, polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

> *For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.*

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO4− can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a polyprotic base that is capable of accepting two protons in a stepwise manner:

$$SO^{2-}_{4(aq)} + H_2O_{(aq)} \rightleftharpoons HSO^-_{4(aq)} + OH^-_{(aq)}$$

$$HSO^-_{4(aq)} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH^-_{(aq)} \tag{17.5.21}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by pK_a + pK_b = pKw. Consider, for example, the HSO^-_4/SO^{2-}_4 conjugate acid–base pair. From Table 17.5.1, we see that the pK_a of HSO^-_4 is 1.99. Hence the pK_b of SO^{2-}_4 is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Equation 17.5.21 lies to the left. The HSO^-_4 ion is also a very weak base (pK_a of H_2SO_4 = 2.0, pK_b of $HSO^-_4 = 14 - (-2.0) = 16$), which is consistent with what we expect for the conjugate base of a strong acid.

Example 17.5.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH^+_{4(aq)} + PO^{3-}_{4(aq)} \rightleftharpoons NH_{3(aq)} + HPO^{2-}_{4(aq)}$
- $CH_3CH_2CO_2H_{(aq)} + CN^-_{(aq)} \rightleftharpoons CH_3CH_2CO^-_{2(aq)} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Tables 17.5.1and17.5.2 and Figure 17.5.2 to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

Solution:

The conjugate acid–base pairs are NH^+_4/NH_3 and HPO^{2-}_4/PO^{3-}_4. According to Tables 17.5.1 and 17.5.2, NH^+_4 is a stronger acid ($pK_a = 9.25$) than HPO^{2-}_4 (pKa = 12.32), and PO^{3-}_4 is a stronger base ($pK_b = 1.68$) than NH_3 ($pK_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH^+_{4(aq)}} + \underset{\text{stronger base}}{PO^{3-}_{4(aq)}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO^{2-}_{4(aq)}}$$

The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO^-_2$ and HCN/CN^-. According to Table 17.5.1, HCN is a weak acid (pKa = 9.21) and CN^- is a moderately weak base (pKb = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table 17.5.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-CH_2CH_3$ versus $-CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN^-_{(aq)}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO^-_{2(aq)}} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

Exercise 17.5.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

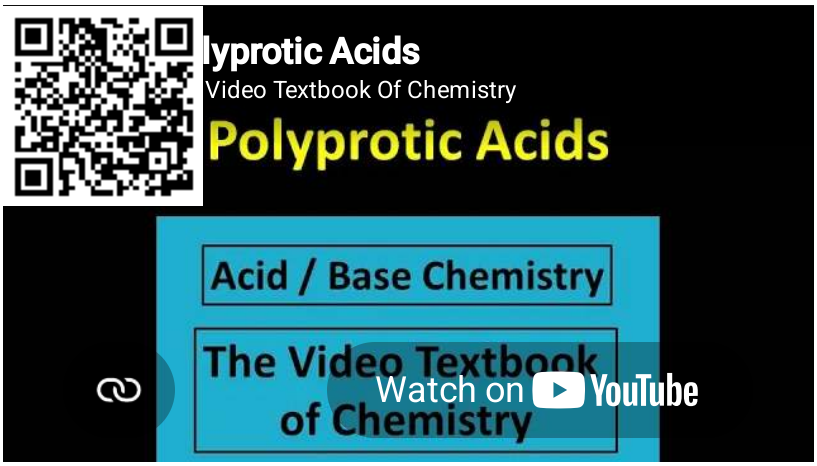
a. $H_2O_{(l)} + HS^-_{(aq)} \rightleftharpoons OH^-_{(aq)} + H_2S_{(aq)}$
b. $HCO^-_{2(aq)} + HSO^-_{4(aq)} \rightleftharpoons HCO_2H_{(aq)} + SO^{2-}_{4(aq)}$

Answer a

left

Answer b

left



A Video Discussing Polyprotic Acids: Polyprotic Acids [youtu.be]

Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (K_a). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (K_b). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w$$

- 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:

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = 14.00 \text{ at } 25°\text{C}$$

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17.6: Autoionization of Water and pH

Learning Objectives

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and pK_w.

As you learned previously acids and bases can be defined in several different ways (Table 17.6.1). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce H^+ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce OH^- (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can donate a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can accept a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton. Consequently, all Brønsted–Lowry acid–base reactions actually involve two conjugate acid–base pairs and the transfer of a proton from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, focuses on accepting or donating pairs of electrons rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

Table 17.6.1: Definitions of Acids and Bases

Definition	Acids	Bases
Arrhenius	H^+ donor	OH^- donor
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Because this chapter deals with acid–base equilibria in aqueous solution, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

Acid–Base Properties of Water

Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the hydronium ion (H_3O^+):

$$\underset{acid}{HCl_{(aq)}} + \underset{base}{H_2O_{(l)}} \rightarrow \underset{acid}{H_3O^+_{(aq)}} + \underset{base}{Cl^-_{(aq)}} \tag{17.6.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation 17.6.1 is often written in a simpler form by removing H_2O from each side:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{17.6.2}$$

In Equation 17.6.2, the hydronium ion is represented by H^+, although free H^+ ions do not exist in liquid water as this reaction demonstrates:

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$$

Water can also act as an acid, as shown in Equation 17.6.3. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{acid}{H_2O_{(l)}} + \underset{base}{NH_{3(aq)}} \rightleftharpoons \underset{acid}{NH^+_{4(aq)}} + \underset{base}{OH^-_{(aq)}} \tag{17.6.3}$$

Water is thus termed amphiprotic, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 17.6.3 is an equilibrium reaction as indicated by the double arrow and hence has an equilibrium constant associated with it.

The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{17.6.4}$$

The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \approx \frac{[H_3O^+][HO^-]}{(1)^2} = [H_3O^+][HO^-] \tag{17.6.5}$$

where a is the activity of a species. Because water is the solvent, and the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The activity of each solute is approximated by the molarity of the solute.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that Ka = $K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation Ka = $K_{eq}(a_{H_2O})$. Because a_{H_2O} = 1 for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and as the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

$$K_w = [H_3O^+][HO^-] \tag{17.6.6}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25 °C, the concentrations of the hydronium ion and the hydroxide ion are equal:

$$[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}\ M \tag{17.6.7}$$

Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb.

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25 °C into this expression

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{17.6.8}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}$ *at room temperature*, and

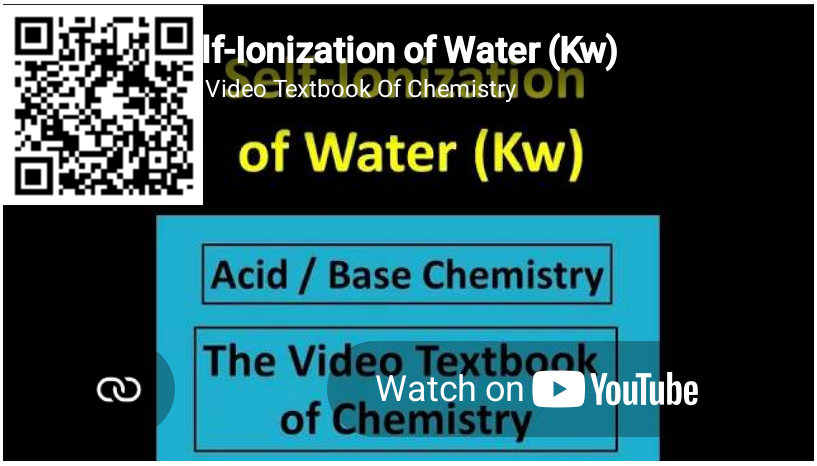
$$K_w = 1.01 \times 10^{-14} = [H_3O^+][OH^-] \tag{17.6.9}$$

.

Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0 °C to 4.99×10^{-13} at 100 °C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the OH^- concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+

and OH^- concentrations from the dissociation of water are so small ($1.003 \times 10^{-7} M$) that they can be ignored in calculating the H_3O^+ or OH^- concentrations of solutions of acids and bases, but this is not always the case.



A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw): [youtu.be]

The Relationship among pH, pOH, and pK_w

The pH scale is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall that pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH = -\log_{10}[H^+] \tag{17.6.10}$$

$$[H^+] = 10^{-pH} \tag{17.6.11}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}\ M$), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous pOH scale to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

$$pOH = -\log_{10}[OH^-] \tag{17.6.12}$$

$$[OH^-] = 10^{-pOH} \tag{17.6.13}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log\ K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25 °C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for any aqueous solution at 25 °C by taking the negative logarithm of both sides of Equation ???:

$$-\log_{10} K_w = pK_w \tag{17.6.14}$$

$$= -\log([H_3O^+][OH^-]) \tag{17.6.15}$$

$$= (-\log[H_3O^+]) + (-\log[OH^-]) \tag{17.6.16}$$

$$= pH + pOH \tag{17.6.17}$$

Thus at any temperature, $pH + pOH = pK_w$, so at 25 °C, where $K_w = 1.0 \times 10^{-14}$, pH + pOH = 14.00. More generally, the pH of any neutral solution is half of the pK_w at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure 17.6.1 over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

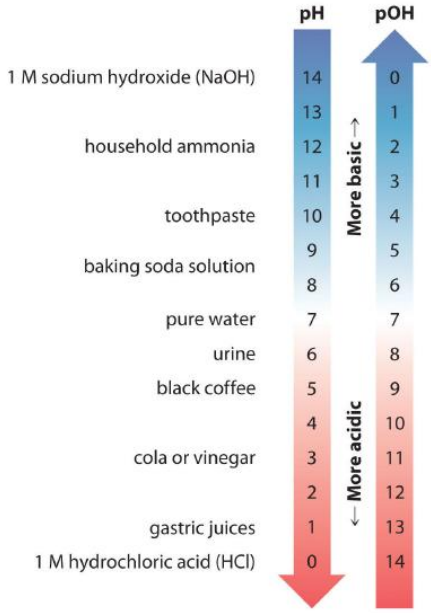
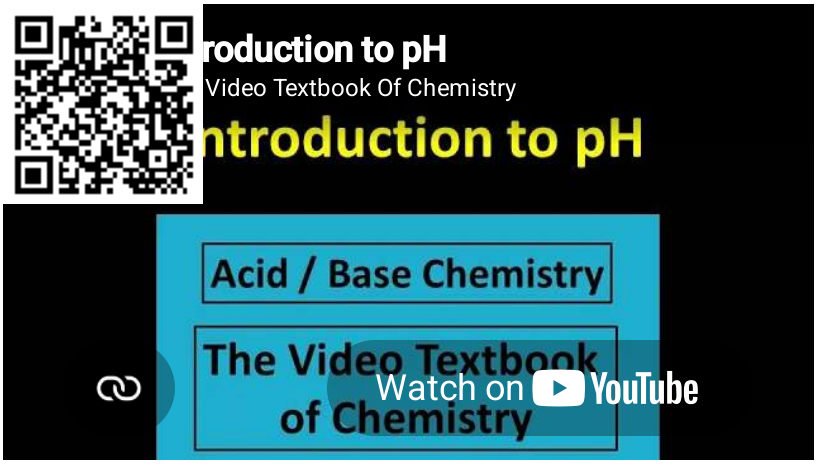


Figure 17.6.1: The Inverse Relationship between the pH and pOH Scales. As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.

Zero is the most acidic and fourteen is the most basic on the pH scale. Zero is the most basic and fourteen is the most acidic on the pOH scale.

> *For any neutral solution, pH + pOH = 14.00 (at 25 °C) with pH=pOH=7.*



A Video Introduction to pH: Introduction to pH [youtu.be]

Example 17.6.1

The K_w for water at 100 °C is 4.99×10^{-13}. Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100 °C. Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w, pH, and pOH

Strategy:

A. Calculate pK_w by taking the negative logarithm of K_w.

B. For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation 17.6.9 to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A

Because pK_w is the negative logarithm of Kw, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12}, so pK_w must be between 12 and 13.

B

Equation ??? shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (x)(x) = x^2 \\ x &= \sqrt{K_w} \\ &= \sqrt{4.99 \times 10^{-13}} \\ &= 7.06 \times 10^{-7}\ M \end{aligned}$$

Because x is equal to both $[H_3O^+]$ and $[OH^-]$,

$$\begin{aligned} pH = pOH &= -\log(7.06 \times 10^{-7}) \\ &= 6.15 \text{ (to two decimal places)} \end{aligned}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w. In this case, we know that $pK_w = 12.302$, and from Equation 17.6.17, we know that $pK_w = pH + pOH$. Because $pH = pOH$ in a neutral solution, we can use Equation 17.6.17 directly, setting $pH = pOH = y$. Solving to two decimal places we obtain the following:

$$\begin{aligned} pK_w &= pH + pOH \\ &= y + y \\ &= 2y \\ y &= \frac{pK_w}{2} \\ &= \frac{12.302}{2} \\ &= 6.15 = pH = pOH \end{aligned}$$

? Exercise 17.6.1

Humans maintain an internal temperature of about 37 °C. At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate pK_w and the pH and the pOH of a neutral solution at 37 °C. Report pH and pOH values to two decimal places.

Answer

- $pK_w = 13.45$
- $pH = pOH = 6.73$

Summary

Water is amphiprotic: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The autoionization of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the ion-product constant of liquid water (Kw) and is defined as $K_w = [H_3O^+][OH^-]$. At 25 °C, K_w is 1.01×10^{-14}; hence $pH + pOH = pK_w = 14.00$.

- For any neutral solution, $pH + pOH = 14.00$ (at 25 °C) and $pH = 1/2pK_w$.
- Ion-product constant of liquid water:

$$K_w = [H_3O^+][OH^-]$$

- Definition of pH:

$$pH = -\log 10[H^+]$$

or

$$[H^+] = 10^{-pH}$$

- Definition of pOH:

$$pOH = -\log_{10}[OH^+]$$

or

$$[OH^-] = 10^{-pOH}$$

- Relationship among pH, pOH, and pK_w:

$$pK_w = pH + pOH$$

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17.7: Finding the [H3O+] and pH of Strong and Weak Acid Solutions

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:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{17.7.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{17.7.2}$$

As we noted earlier, because water is the solvent, it has an activity equal to 1, so the $[H_2O]$ term in Equation 17.7.2 is actually the a_{H_2O}, which is equal to 1.

Again, for simplicity, H_3O^+ can be written as H^+ in Equation 17.7.3.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \tag{17.7.3}$$

Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form hydronium ions, H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them unitless. The values of K_a for a number of common acids are given in Table 17.7.1.

Table 17.7.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{17.7.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{17.7.5}$$

Once again, the activity of water has a value of 1, so water does not appear in the equilibrium constant expression. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 17.7.2.

Table 17.7.2: 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 17.7.1.

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:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{17.7.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{17.7.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{17.7.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{17.7.9}$$

If we add Equations 17.7.6 and 17.7.7, we obtain the following:

add Equations 17.7.6 and 17.7.7, we obtain

Reaction	Equilibrium Constants
$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}}$	$K_a = [H^+]\,\cancel{[CN^-]} \,/\, \cancel{[HCN]}$
$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}}$	$K_b = [OH^-]\,\cancel{[HCN]} \,/\, \cancel{[CN^-]}$
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	$K = K_a \times K_b = [H^+][OH^-]$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{17.7.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{17.7.11}$$

$$K_a = 10^{-pK_a} \tag{17.7.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{17.7.13}$$

$$K_b = 10^{-pK_b} \tag{17.7.14}$$

Similarly, Equation 17.7.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{17.7.15}$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \tag{17.7.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Tables 17.7.1 and 17.7.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

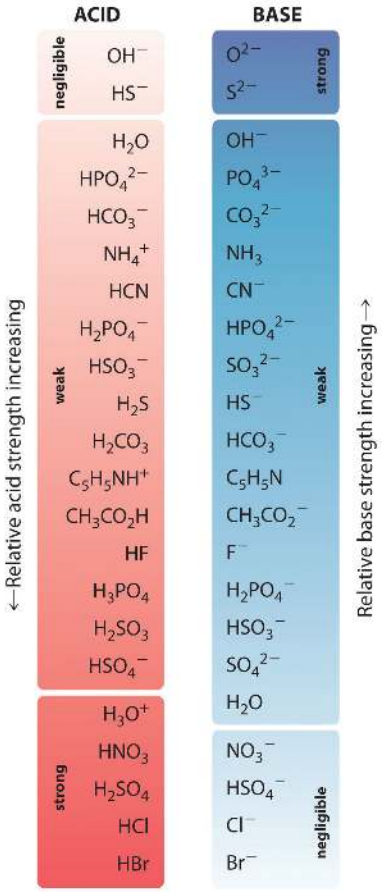


Figure 17.7.1: The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Strong acids are H3O plus, HNO3, H2SO4, HCl, and HBr. Negligible acids are HS minus and OH minus. Stron bases are O negative 2, S negative 2. Negligible bases are NO3 minus, HSO4 minus, Cl minus, and Br minus.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 17.7.1. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This

order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 17.7.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

> *The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{17.7.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_{2(aq)}{}^-}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

> *All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

Example 17.7.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.

b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 17.7.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equations 17.7.15 and 17.7.16. Use the relationships pK = −log K and K = 10^{-pK} (Equations 17.7.11 and 17.7.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 17.7.16: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 17.7.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

? Exercise 17.7.1: 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

- $K_a = 1.4 \times 10^{-4}$ for lactic acid;
- pK_b = 10.14 and
- $K_b = 7.2 \times 10^{-11}$ for the lactate ion



A Video Calculating pH in Strong Acid or Strong Base Solutions: Calculating pH in Strong Acid or Strong Base Solutions [youtu.be]

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 17.7.1 that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which

means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I− or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table 17.7.1 were determined using measurements like this and different nonaqueous solvents.

> *In aqueous solutions, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.*

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH− is leveled to the strength of OH− because OH− is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 17.7.2, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{17.7.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{17.7.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{17.7.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

As you learned, polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

> *For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.*

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO4− can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a polyprotic base that is capable of accepting two protons in a stepwise manner:

$$SO_{4(aq)}^{2-} + H_2O_{(aq)} \rightleftharpoons HSO_{4(aq)}^{-} + OH_{(aq)}^{-}$$

$$HSO_{4(aq)}^{-} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH_{(aq)}^{-} \tag{17.7.21}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by pK_a + pK_b = pKw. Consider, for example, the HSO_4^-/SO_4^{2-} conjugate acid–base pair. From Table 17.7.1, we see that the pK_a of HSO_4^- is 1.99. Hence the pK_b of SO_4^{2-} is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Equation 17.7.21 lies to the left. The HSO_4^- ion is also a very weak base (pK_a of H_2SO_4 = 2.0, pK_b of $HSO_4^- = 14 - (-2.0) = 16$), which is consistent with what we expect for the conjugate base of a strong acid.

Example 17.7.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH_{4(aq)}^{+} + PO_{4(aq)}^{3-} \rightleftharpoons NH_{3(aq)} + HPO_{4(aq)}^{2-}$
- $CH_3CH_2CO_2H_{(aq)} + CN_{(aq)}^{-} \rightleftharpoons CH_3CH_2CO_{2(aq)}^{-} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Tables 17.7.1and17.7.2 and Figure 17.7.2 to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

Solution:

The conjugate acid–base pairs are NH_4^+/NH_3 and HPO_4^{2-}/PO_4^{3-}. According to Tables 17.7.1 and 17.7.2, NH_4^+ is a stronger acid ($pK_a = 9.25$) than HPO_4^{2-} (pKa = 12.32), and PO_4^{3-} is a stronger base ($pK_b = 1.68$) than NH_3 ($pK_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH_{4(aq)}^{+}} + \underset{\text{stronger base}}{PO_{4(aq)}^{3-}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO_{4(aq)}^{2-}}$$

The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$ and HCN/CN^-. According to Table 17.7.1, HCN is a weak acid (pKa = 9.21) and CN^- is a moderately weak base (pKb = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table 17.7.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-CH_2CH_3$ versus $-CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN_{(aq)}^{-}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO_{2(aq)}^{-}} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

Exercise 17.7.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

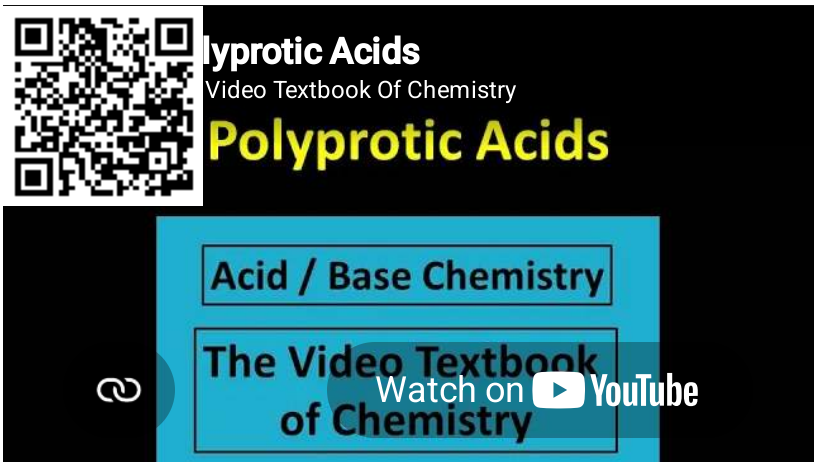
a. $H_2O_{(l)} + HS_{(aq)}^{-} \rightleftharpoons OH_{(aq)}^{-} + H_2S_{(aq)}$
b. $HCO_{2(aq)}^{-} + HSO_{4(aq)}^{-} \rightleftharpoons HCO_2H_{(aq)} + SO_{4(aq)}^{2-}$

Answer a

left

Answer b

left



A Video Discussing Polyprotic Acids: Polyprotic Acids [youtu.be]

Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (K_a). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (K_b). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w$$

- 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:

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = 14.00 \text{ at } 25°C$$

Contributors and Attributions

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17.8: Finding the [OH-] and pH of Strong and Weak Base Solutions



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17.9: The Acid-Base Properties of Ions and Salts

Learning Objectives

- To recognize salts that will produce acidic, basic, or neutral solutions in water
- To understand the Lewis acidity of small, highly-charged metal ions in water

A neutralization reaction can be defined as the reaction of an acid and a base to produce a salt and water. That is, another cation, such as Na^+, replaces the proton on the acid. An example is the reaction of CH_3CO_2H, a weak acid, with $NaOH$, a strong base:

$$\underset{acid}{CH_3CO_2H_{(l)}} + \underset{base}{NaOH_{(s)}} \xrightarrow{H_2O} \underset{salt}{H_2OCH_3CO_2Na_{(aq)}} + \underset{water}{H_2O_{(l)}}$$

Depending on the acid–base properties of its component ions, however, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as $NaCl$ dissolves in water, it produces $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ ions. Using a Lewis approach, the Na^+ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a very weak acid. The Cl^- ion is the conjugate base of the strong acid HCl, so it has essentially no basic character. Consequently, dissolving $NaCl$ in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations (K^+ and Na^+) have essentially no acidic character, but the anions (CN^- and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively.

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

$$CH_3CO^2_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$$

Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table 17.9.1 and Figure 17.9.1, we can see that CN^- is a stronger base ($pK_b = 4.79$) than acetate ($pK_b = 9.24$), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid (Equation 17.9.1). For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water as follows:

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons HH_{3(aq)} + H_3O^+_{(aq)} \tag{17.9.1}$$

$$C_5H_5NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons C_5H_5NH_{(aq)} + H_3O^+_{(aq)} \tag{17.9.2}$$

Equation 17.9.1 indicates that H_3O^+ is a stronger acid than either NH_4^+ or $C_5H_5NH^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The H_3O^+ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at 25°C is 5.13 or 3.12, respectively. This is consistent with the information shown in Figure 16.2, indicating that the pyridinium ion is more acidic than the ammonium ion.

What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation and the anion can react separately with water to produce an acid and a base, respectively? According to Figure 16.10, the ammonium ion will lower the pH, while according to Equation 17.9.2, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base (pKa ≈ pKb). Consequently, the two effects cancel, and the solution remains neutral. With salts in which the

cation is a stronger acid than the anion is a base, the final solution has a $pH < 7.00$. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a $pH > 7.00$.

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (part (a) in Figure 17.9.1). A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

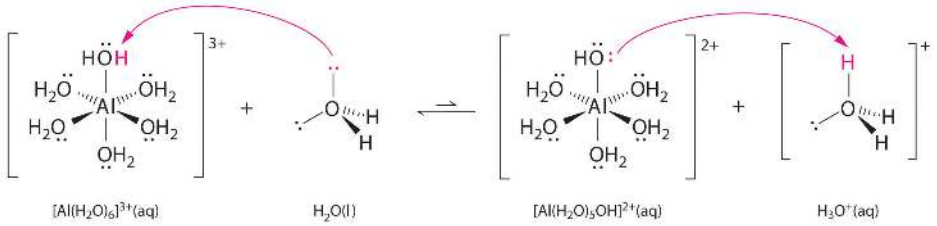


Figure 17.9.1. With less electron density between the O atoms and the H atoms, the O–H bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion.

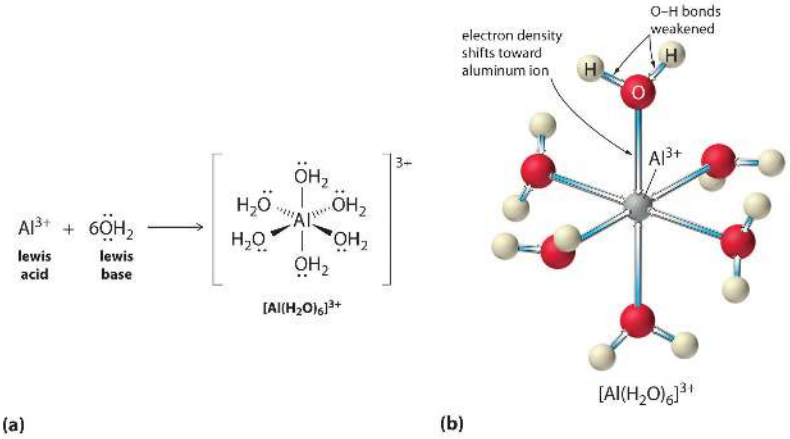


Figure 17.9.1: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.

On the left is the reaction of Al three plus with six OH2 which produces [AL(H2O)6] three plus. On the right is the molecular structure of [Al(H2O)6] three plus.

The magnitude of this effect depends on the following two factors (Figure 17.9.2):

1. The charge on the metal ion. A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^+) of the same radius.
2. The radius of the metal ion. For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

Figure 17.9.2: The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.

Thus aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{17.9.3}$$

The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the charge-to-radius ratio of the metal ion. A number of pairs of metal ions that lie on a diagonal line in the periodic table, such as Li^+ and Mg^{2+} or Ca^{2+} and Y^{3+}, have different sizes and charges, but similar charge-to-radius ratios. As a result, these pairs of metal ions have similar effects on the acidity of coordinated water molecules, and they often exhibit other significant similarities in chemistry as well.

> *Solutions of small, highly charged metal ions in water are acidic.*

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactions. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

> *A hydrolysis reaction is an acid–base reaction.*

Example 17.9.1

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

a. KNO_3
b. $CrBr_3 cdot H_2O$
c. Na_2SO_4

Given: compound

Asked for: acidity or basicity of aqueous solution

Strategy:

A. Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.
B. f the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

Solution:

a

A. The K^+ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so it is a very weak Lewis acid.

B. The NO_3- anion is the conjugate base of a strong acid, so it has essentially no basic character (Table 16.1). Hence neither the cation nor the anion will react with water to produce H^+ or OH^-, and the solution will be neutral.

b.

A. The Cr^{3+} ion is a relatively highly charged metal cation that should behave similarly to the Al^{3+} ion and form the $[Cr(H2O)_6]^{3+}$ complex, which will behave as a weak acid:

$$Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)}$$

B. The Br^- anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution. Hence the solution will be acidic.

c.

A. The Na^+ ion, like the K^+, is a very weak acid, so it should not affect the acidity of the solution.
B. In contrast, SO_4^{2-} is the conjugate base of HSO_4^-, which is a weak acid. Hence the SO_4^{2-} ion will react with water as shown in Figure 16.6 to give a slightly basic solution.

Exercise 17.9.1

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

a. KI
b. $Mg(ClO_4)_2$
c. $NaHS$

Answer a

neutral

Answer b

acidic

Answer c

basic (due to the reaction of HS^- with water to form H_2S and OH^-)

Summary

A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the conjugate base of a weak acid as the anion (A^-), the conjugate acid of a weak base as the cation (BH^+), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a hydrolysis reaction.

Key Takeaways

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

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17.10: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

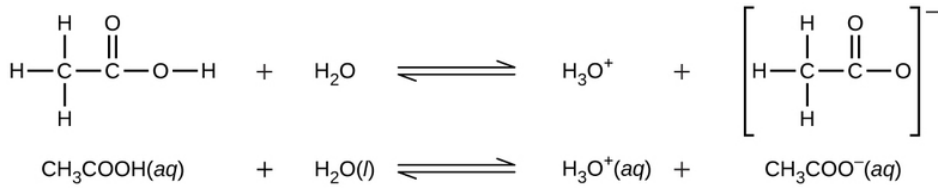
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $\mathrm{HNO_3}$, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$

$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq)$$

$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq)$$

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, $\mathrm{H_2CO_3}$, 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**

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq)$$

with

$$K_{\mathrm{H_2CO_3}} = \frac{[H3O+][HCO3-]}{[H2CO3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq)$$

with

$$K_{\mathrm{HCO_3^-}} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = 4.7 \times 10^{-11}$$

$K_{\mathrm{H_2CO_3}}$ is larger than $K_{\mathrm{HCO_3^-}}$ by a factor of 10^4, so $\mathrm{H_2CO_3}$ is the dominant producer of hydronium ion in the solution. This means that little of the $\mathrm{HCO_3^-}$ formed by the ionization of $\mathrm{H_2CO_3}$ ionizes to give hydronium ions (and carbonate ions), and the concentrations of $\mathrm{H_3O^+}$ and $\mathrm{HCO_3^-}$ are practically equal in a pure aqueous solution of $\mathrm{H_2CO_3}$.

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 $\mathrm{H_3O^+}$ 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 17.10.1: 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 $\mathrm{CO_2}$ reacts with water to form carbonic acid, $\mathrm{H_2CO_3}$. What are $[\mathrm{H_3O^+}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{CO_3^{2-}}]$ in a saturated solution of $\mathrm{CO_2}$ with an initial $[\mathrm{H_2CO_3}] = 0.033\ M$?

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

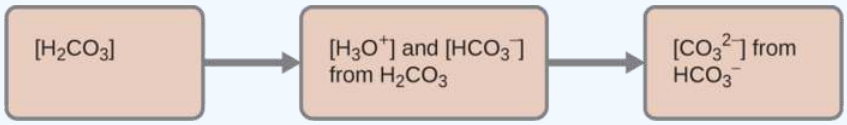
$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{\mathrm{a2}} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, $\mathrm{H_2CO_3}$ is a much stronger acid than $\mathrm{HCO_3^-}$, so $\mathrm{H_2CO_3}$ 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 $\mathrm{H_3O^+}$ and $\mathrm{HCO_3^-}$ produced by ionization of $\mathrm{H_2CO_3}$.
2. Then we determine the concentration of $\mathrm{CO_3^{2-}}$ in a solution with the concentration of $\mathrm{H_3O^+}$ and $\mathrm{HCO_3^-}$ determined in (1).

To summarize:



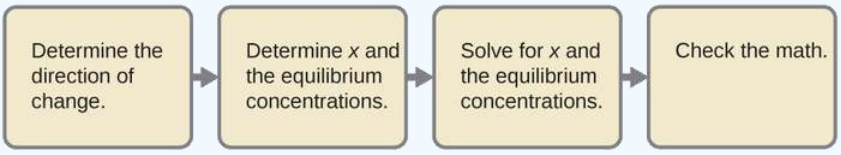
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right 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	$H_2CO_3(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$HCO_3^-(aq)$
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:

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-\ ] = 1.2 \times 10^{-4}\ M$$

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:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
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

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[CO_3^{2-}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the H_2CO_3 in a 0.033-M solution ionizes slightly and at equilibrium $[H_2CO_3] = 0.033\ M$, $[H_3O^+] = 1.2 \times 10^{-4}$, and $[HCO_3^-] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[CO_3^{2-}] = 5.6 \times 10^{-11}\ M$.

? Exercise 17.10.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 1.0 \times 10^{-19}$$

Answer

$[H_2S] = 0.1M$, $[H_3O^+] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

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).

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**

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

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:

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

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

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17.11: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an electron-pair transfer reaction, clearly identifying the donor and acceptor.
- Give an example of a *Lewis acid-base reaction* that does not involve protons.
- Write equations illustrating the behavior of a given non-aqueous acid-base system.

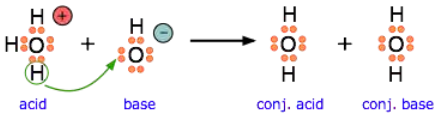
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. According to Lewis,

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Proton-Transfer Reactions Involve Electron-Pair Transfer

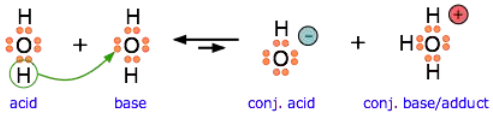
Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



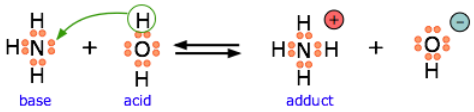
This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note carefully that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

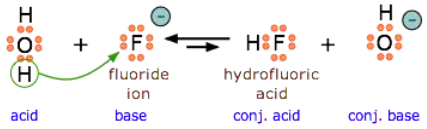
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product of a Lewis acid-base reaction is known formally as an "adduct" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.



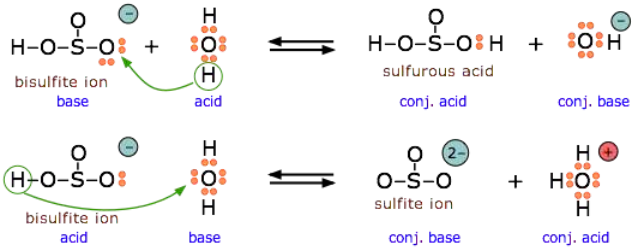
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.



The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

Acid-base Reactions without Transferring Protons

The major utility of the Lewis definition is that it extends the concept of acids and bases beyond the realm of proton transfer reactions. The classic example is the reaction of boron trifluoride with ammonia to form an *adduct*:

$$BF_3 + NH_3 \rightarrow F_3B{-}NH_3 \tag{17.11.1}$$

One of the most commonly-encountered kinds of Lewis acid-base reactions occurs when electron-donating ligands form coordination complexes with transition-metal ions.

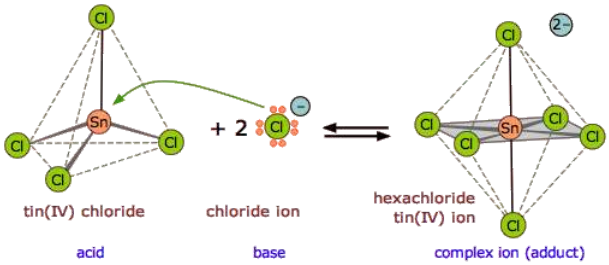


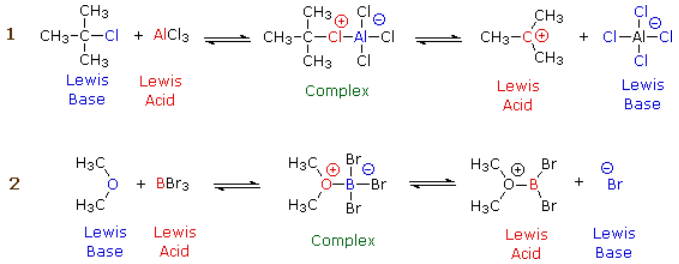
Figure 17.11.1: The tin atom in $SnCl_4$ can expand its valence shell by utilizing a pair of d-orbitals, changing its hybridization from sp^3 to sp^3d^2.

? Exercise 17.11.1

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2\,CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $Ni^{2+} + 6\,NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Although organic chemistry is beyond the scope of these lessons, it is instructive to see how electron donors and acceptors play a role in chemical reactions. The following two diagrams show the mechanisms of two common types of reactions initiated by simple inorganic Lewis acids:



In each case, the species labeled "Complex" is an intermediate that decomposes into the products, which are conjugates of the original acid and base pairs. The electric charges indicated in the complexes are formal charges, but those in the products are "real".

In reaction 1, the incomplete octet of the aluminum atom in $AlCl_3$ serves as a better electron acceptor to the chlorine atom than does the isobutyl part of the base. In reaction 2, the pair of non-bonding electrons on the dimethyl ether coordinates with the electron-deficient boron atom, leading to a complex that breaks down by releasing a bromide ion.

Non-aqueous Protonic Acid-Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table 17.11.1). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. However, many other familiar substances can also serve as the basis of protonic solvent systems as Table 17.11.1 indicates:

Table 17.11.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_{ap}
water	$2\,H_2O \rightarrow H_3O^+ + OH^-$	14
ammonia	$2\,NH_3 \rightarrow NH_4^+ + NH_2^-$	33
acetic acid	$2\,CH_3COOH \rightarrow CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2\,C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2\,HO\text{-}OH \rightarrow HO\text{-}OH_2^+ + HO\text{-}O^-$	13
hydrofluoric acid	$2\,HF \rightarrow H_2F^+ + F^-$	10
sulfuric acid	$2\,H_2SO_4 \rightarrow H_3SO_4^+ + HSO_4^-$	3.5

One use of nonaqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined.

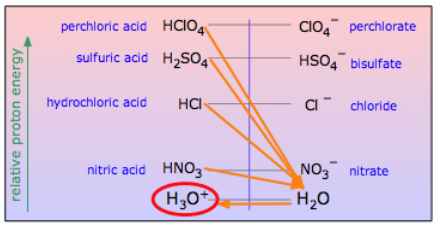


Figure 17.11.2: Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling" of the solvent.

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CHAPTER OVERVIEW

18: Aqueous Ionic Equilibrium

Topic hierarchy

18.1: The Danger of Antifreeze
18.2: Buffers- Solutions That Resist pH Change
18.3: Buffer Effectiveness- Buffer Capacity and Buffer Range
18.4: Titrations and pH Curves
18.5: Solubility Equilibria and the Solubility Product Constant
18.6: Precipitation
18.7: Complex Ion Equilibria

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18.1: The Danger of Antifreeze

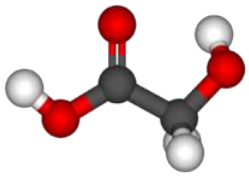
An antifreeze is an additive which lowers the freezing point of a water-based liquid. An antifreeze mixture is used to achieve freezing-point depression for cold environments and also achieves boiling-point elevation to allow higher coolant temperature. Freezing and boiling points are colligative properties of a solution, which depend on the concentration of the dissolved substance. Because water has good properties as a coolant, water plus antifreeze is used in internal combustion engines and other heat transfer applications. The purpose of antifreeze is to prevent a rigid enclosure from bursting due to expansion when water freezes. Commercially, both the additive (pure concentrate) and the mixture (diluted solution) are called antifreeze, depending on the context. Careful selection of an antifreeze can enable a wide temperature range in which the mixture remains in the liquid phase, which is critical to efficient heat transfer and the proper functioning of heat exchangers.



Fluorescent green-dyed antifreeze is visible in the radiator header tank when car radiator cap is removed. (CC BY-SA 2.0; EvelynGiggles)

Ethylene glycol solutions became available in 1926 and were marketed as "permanent antifreeze" since the higher boiling points provided advantages for summertime use as well as during cold weather. They are used today for a variety of applications, including automobiles, but gradually being replaced by propylene glycol due to its lower toxicity.

When ethylene glycol is used in a system, it may become oxidized to five organic acids (formic, oxalic, glycolic, glyoxalic and acetic acid). Inhibited ethylene glycol antifreeze mixes are available, with additives that buffer the pH and reserve alkalinity of the solution to prevent oxidation of ethylene glycol and formation of these acids. Nitrites, silicates, theodin, borates and azoles may also be used to prevent corrosive attack on metal.



Glycolic acid is the major metabolite of ethylene glycol responsible for toxicity. (Public Domain).

Ethylene glycol is poisonous to humans and other animals,[4][5] and should be handled carefully and disposed of properly. Its sweet taste can lead to accidental ingestion or allow its deliberate use as a murder weapon.[6][7][8] Ethylene glycol is difficult to detect in the body, and causes symptoms—including intoxication, severe diarrhea, and vomiting—that can be confused with other illnesses or diseases.[4][8] Its metabolism produces calcium oxalate, which crystallizes in the brain, heart, lungs, and kidneys, damaging them; depending on the level of exposure, accumulation of the poison in the body can last weeks or months before causing death, but death by acute kidney failure can result within 72 hours if the individual does not receive appropriate medical treatment for the poisoning.[4] Some ethylene glycol antifreeze mixtures contain an embittering agent, such as denatonium, to discourage accidental or deliberate consumption.

The toxic mechanism of ethylene glycol poisoning is mainly due to the metabolites of ethylene glycol. Initially it is metabolized by alcohol dehydrogenase to glycolaldehyde, which is then oxidized to glycolic acid.[7] The increase in metabolites may cause encephalopathy or cerebral edema.[13] The metabolic effects occur 12 to 36 hours post ingestion, causing primarily metabolic acidosis which is due mainly to accumulated glycolic acid. Additionally, as a side effect of the first two steps of metabolism, an increase in the blood concentration of lactic acid occurs contributing to lactic acidosis. The formation of acid metabolites also causes inhibition of other metabolic pathways, such as oxidative phosphorylation.[7]

The kidney toxicity of ethylene glycol occurs 24 to 72 hours post ingestion and is caused by a direct cytotoxic effect of glycolic acid. The glycolic acid is then metabolized to glyoxylic acid and finally to oxalic acid. Oxalic acid binds with calcium to form calcium oxalate crystals which may deposit and cause damage to many areas of the body including the brain, heart, kidneys, and lungs.[7] The most significant effect is accumulation of calcium oxalate crystals in the kidneys which causes kidney damage leading to oliguric or anuric acute kidney failure.[7] The rate-limiting step in this cascade is the conversion of glycolic to glyoxylic acid.[14] Accumulation of glycolic acid in the body is mainly responsible for toxicity.[15]

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18.2: Buffers- Solutions That Resist pH Change

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:

$$[Na^+] + [K^+] = [Cl^-] \tag{18.2.1}$$

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.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$KCl \rightleftharpoons K^+ + Cl^-$$

$$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$$

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

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, $[Cl^-]$ differs from $[Ag^+]$. The following examples show how the concentration of the common ion is calculated.

Example 18.2.1

What are $[Na^+]$, $[Cl^-]$, $[Ca^{2+}]$, and $[H^+]$ in a solution containing 0.10 M each of $NaCl$, $CaCl_2$, and HCl?

Solution

Due to the conservation of ions, we have

$$[Na^+] = [Ca^{2+}] = [H^+] = 0.10\ M$$

but

$$\begin{aligned}[Cl^-] = &\ 0.10\ (\text{due to NaCl}) \\ &+ 0.20\ (\text{due to } CaCl_2) \\ &+ 0.10\ (\text{due to HCl}) \\ = &\ 0.40\ M\end{aligned}$$

Exercise 18.2.1

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 $[Cl^-]$ in the final solution?

Solution

$$[Cl^-] = \frac{0.1\ M \times 10\ mL + 0.2\ M \times 5.0\ mL}{100.0\ mL} = 0.020\ M$$

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 18.2.2: Solubility of Lead Chloride

Consider the lead(II) ion concentration in this *saturated* solution of $PbCl_2$. The balanced reaction is

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$K_{sp} = [Pb^{2+}][Cl^-]^2 \tag{18.2.2}$$
$$= s \times (2s)^2 \tag{18.2.3}$$
$$1.7 \times 10^{-5} = 4s^3 \tag{18.2.4}$$
$$s^3 = \frac{1.7 \times 10^{-5}}{4} \tag{18.2.5}$$
$$= 4.25 \times 10^{-6} \tag{18.2.6}$$
$$s = \sqrt[3]{4.25 \times 10^{-6}} \tag{18.2.7}$$
$$= 1.62 \times 10^{-2}\ mol\ dm^{-3} \tag{18.2.8}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:

$$PbCl_2\ (s) \rightleftharpoons Pb^{2+}\ (aq) + 2Cl^-\ (aq)$$

What happens to that equilibrium if extra chloride ions are added? According to *Le* Châtelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

Example 18.2.3

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.

$$[Pb^{2+}] = s \tag{18.2.9}$$

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:

$$[Cl^-] = 0.100\ M \tag{18.2.10}$$

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:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\,\text{M} \end{aligned} \tag{18.2.11}$$

Finally, compare that value with the simple saturated solution:

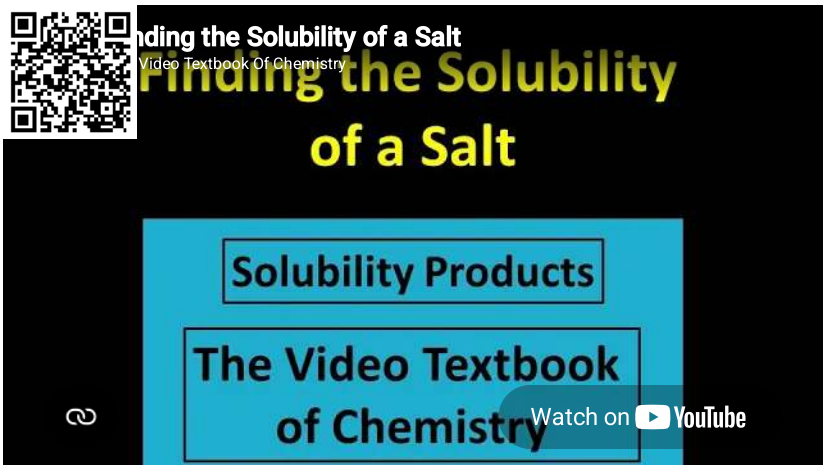
Original solution:

$$[Pb^{2+}] = 0.0162\ M \tag{18.2.12}$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M \tag{18.2.13}$$

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.



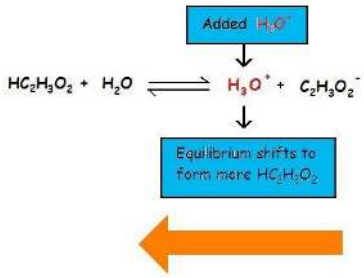
A Video Discussing Finding the Solubility of a Salt: Finding the Solubility of a Salt(opens in new window) [youtu.be]

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.*

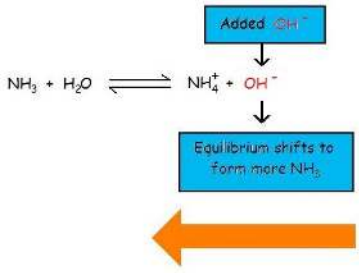
The common ion effect of H_3O^+ on the ionization of acetic acid



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 H_3O^+ the equilibrium shifts to form more $HC_2H_3O_2$.

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 OH^- on the ionization of ammonia



When a strong base supplies the common ion OH^- the equilibrium shifts to form more 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.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq) \tag{18.2.14}$$

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

$$K = \frac{[Ca^{2+}]^3[PO_4^{3-}]^2}{[Ca_3(PO_4)_2]} \tag{18.2.15}$$

$$[Ca_3(PO_4)_2]K = K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 \tag{18.2.16}$$

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 18.2.15, 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 18.2.15 (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 $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 18.2.15 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 18.2.5

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 $(s)(2s)^2 = 1.7\times10^{-5}$. Solving the equation for s gives $s = 1.62\times10^{-2}$ 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.

$$Q_{sp} = [Pb^{2+}][Cl^-]^2 \tag{18.2.17}$$
$$1.8 \times 10^{-5} = (s)(2s + 0.1)^2 \tag{18.2.18}$$
$$s = [Pb^{2+}] \tag{18.2.19}$$
$$= 1.8 \times 10^{-3} M \tag{18.2.20}$$
$$2s = [Cl^-] \tag{18.2.21}$$
$$\approx 0.1M \tag{18.2.22}$$

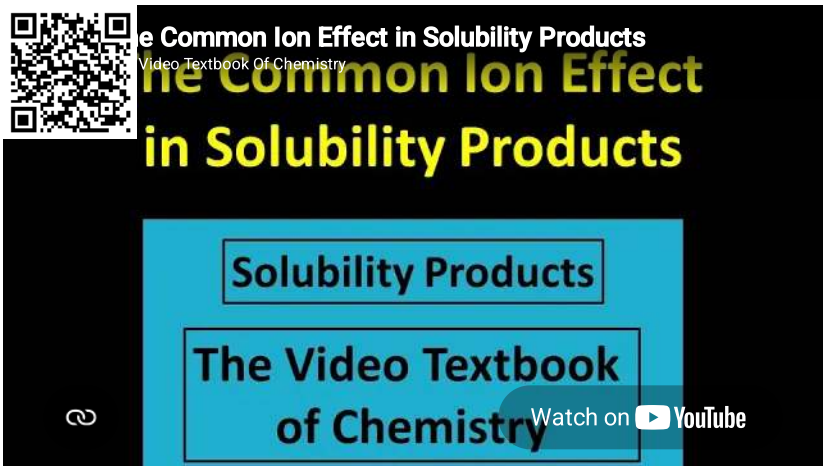
Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[Cl^-]$ is approximately 0.1M since the formation of the chloride ion from the dissociation 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 18.2.5

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)



A Video Discussing the Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products (opens in new window) [youtu.be]

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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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:

$$\mathrm{CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)} \tag{18.2.23}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3CO_2H}]} \tag{18.2.24}$$

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 18.2.23 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 18.2.1

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 $\mathrm{Na^+}$ 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,

$$K_aC_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

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 $\mathrm{H^+}$ 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 $[HCO_2^-]$. 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 18.2.1

A 0.225 M solution of ethylamine ($CH_3CH_2NH_2$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

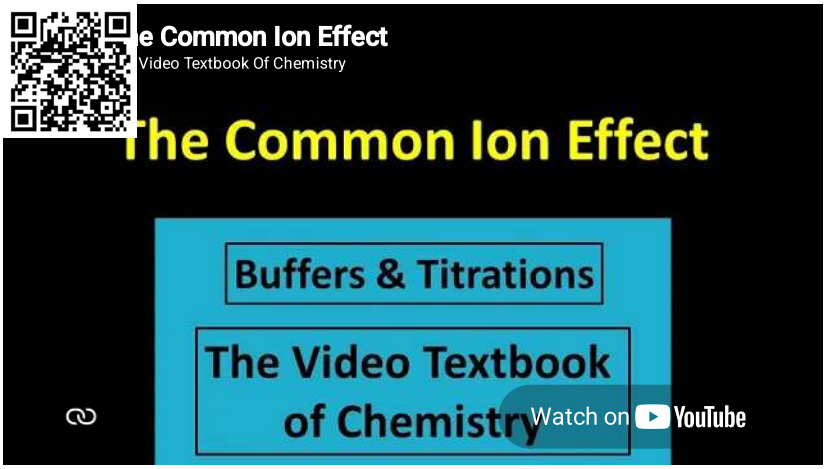
a. the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
b. the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

Answer a

11.16

Answer b

1.3%



A Video Discussing the Common Ion Effect: The Common Ion Effecr(opens in new window) [youtu.be]

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:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \tag{18.2.25}$$

If the equilibrium constant for the reaction as written in Equation 18.2.25 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \frac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 18.2.25 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 5.0, 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:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{18.2.26}$$

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 18.2.26 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 18.2.1, 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.

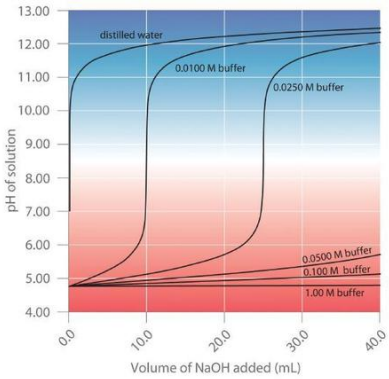


Figure 18.2.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

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 18.2.1 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:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{18.2.27}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{18.2.28}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{18.2.29}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{18.2.30}$$

Replacing the negative logarithms in Equation 18.2.30,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{18.2.31}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{18.2.32}$$

Equation 18.2.31 and Equation 18.2.32 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 18.2.32. 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 18.2.32, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$
- $[base]/[acid] = 100$: In Equation 18.2.32, 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 18.2.2

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 18.2.31 or 18.2.32) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 18.2.31), 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 18.2.32, 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 18.2.2

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?

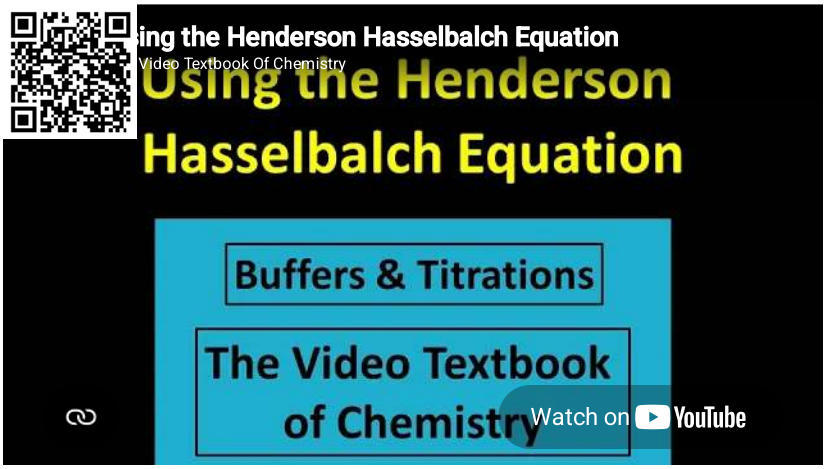
The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68



A Video Discussing Using the Henderson Hasselbalch Equation: Using the Henderson Hasselbalch Equation(opens in new window) [youtu.be] (opens in new window)

The Henderson-Hasselbalch approximation ((Equation 18.2.31) 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 18.2.3.

Example 18.2.3

The buffer solution in Example 18.2.2 contained 0.135 M HCO_2H and 0.215 M 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 18.2.1. 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 18.2.32) 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:

$$100 \cancel{mL}\left(\frac{0.135\,mmol\ HCO_2H}{\cancel{mL}}\right) = 13.5\,mmol\,HCO_2H$$

$$100 \cancel{mL}\left(\frac{0.215\,mmol\ HCO_2^-}{\cancel{mL}}\right) = 21.5\,mmol\,{}_2HCO^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00 \cancel{mL}\left(\frac{1.00\,mmol\ H^+}{\cancel{mL}}\right) = 5\,mmol\,H^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$HCO^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_2H(aq)$$

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 18.2.1 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 18.2.32):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

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 18.2.3

The buffer solution from Example 18.2.2 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?

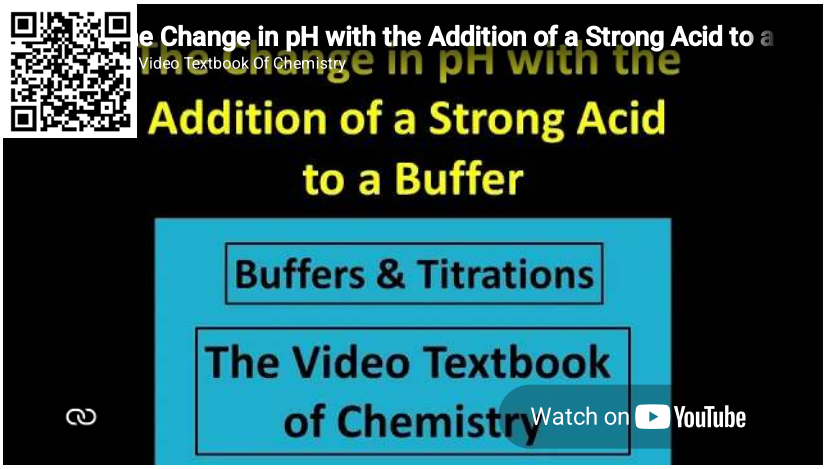
Answer a

5.30

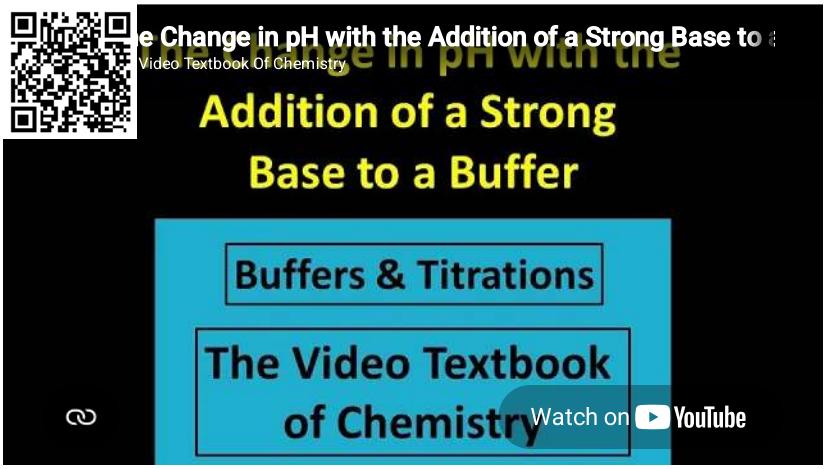
Answer b

4.42

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.



A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: The Change in pH with the Addition of a Strong Acid to a Buffer(opens in new window) [youtu.be]



The Change in pH with the Addition of a Strong Base to a Buffer:

The Change in pH with the Addition of a Strong Base to a Buffer (opens in new window) [youtu.be]

The results obtained in Example 18.2.3 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 18.2.2 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.

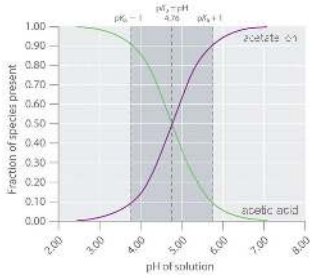
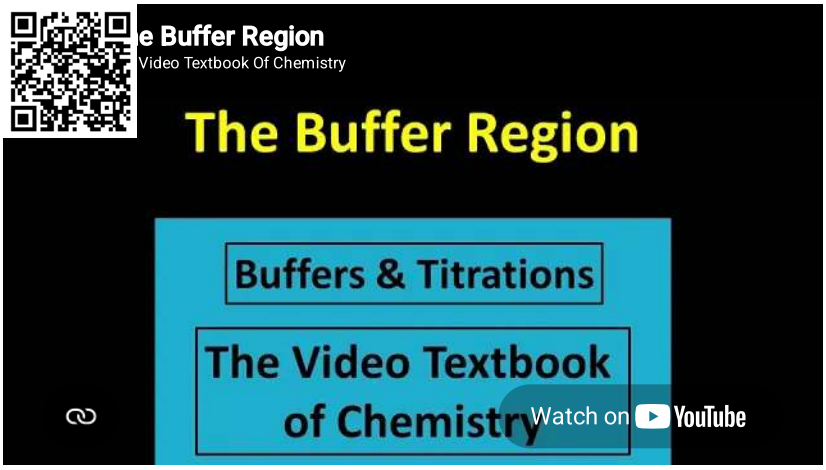


Figure 18.2.2: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable 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.



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 18.2.3. 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.

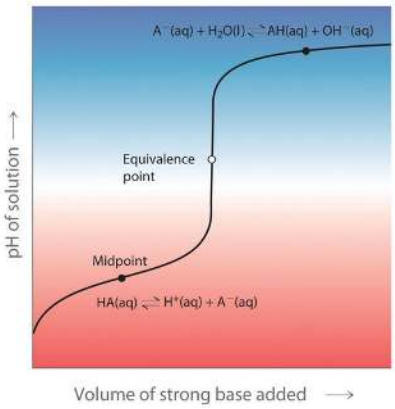


Figure 18.2.3: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

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:

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{18.2.33}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 18.2.33 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 18.2.33 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 18.2.34, 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:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \tag{18.2.34}$$

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 18.2.33 suggests. Adding Equation 18.2.33 and Equation 18.2.34 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:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \tag{18.2.35}$$

with $K' = 4.0 \times 10^{-3} (37°C)$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{18.2.36}$$

with $K_a = 2.0 \times 10^{-4} (37°C)$

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{18.2.37}$$

with $K = 8.0 \times 10^{-7} (37°C)$

The K value for the reaction in Equation 18.2.37 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

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{18.2.38}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to **Henry's law**,

$$[CO_2] = kP_{CO_2}$$

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 18.2.38,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{18.2.39}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 18.2.4 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.

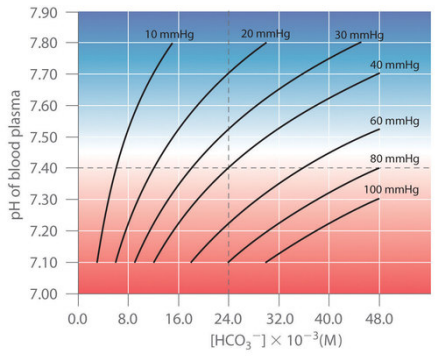
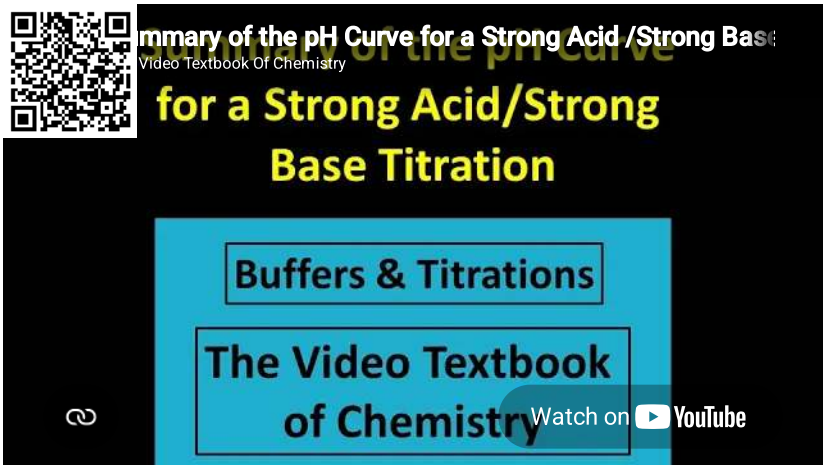


Figure 18.2.4: Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 18.2.39, 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 18.2.39 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.



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.

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18.3: Buffer Effectiveness- Buffer Capacity and Buffer Range

Buffer Capacity

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 18.3.1, 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.

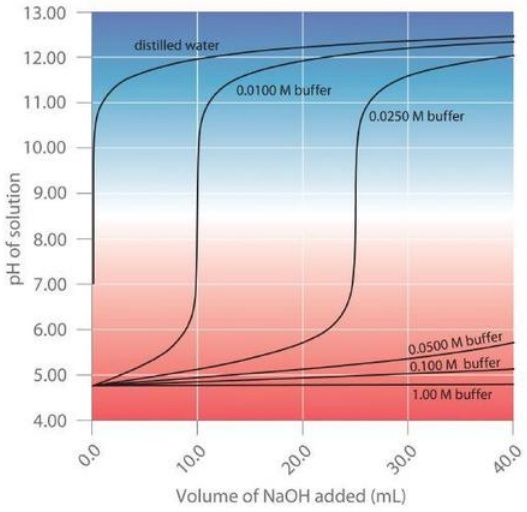


Figure 18.3.1***:*** *Effect of Buffer Concentration on the Capacity of a Buffer*

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.

Selecting proper components for desired pH

Buffers function best when the pK_a of the conjugate weak acid used is close to the desired working range of the buffer. This turns out to be the case when the concentrations of the conjugate acid and conjugate base are approximately equal (within about a factor of 10). For example, we know the K_a for hydroflouric acid is 6.6×10^{-4} so its $pK_a = -\log(6.6 \times 10^{-4}) = 3.18$. So, a hydrofluoric acid buffer would work best in a buffer range of around pH = 3.18.

For the weak base ammonia (NH_3), the value of K_b is 1.8×10^{-5}, implying that the K_a for the dissociation of its conjugate acid, NH_4^+, is $K_w/K_b = 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$. Thus, the pK_a for $NH_4^+ = 9.25$, so buffers using NH_4^+/NH_3 will work best around a pH of 9.25. (It's always the pK_a of the conjugate acid that determines the approximate pH for a buffer system, though this is dependent on the pK_b of the conjugate base, obviously.)

When the desired pH of a buffer solution is near the pK_a of the conjugate acid being used (i.e., when the amounts of conjugate acid and conjugate base in solution are within about a factor of 10 of each other), the Henderson-Hasselbalch equation can be applied as a simple approximation of the solution pH, as we will see in the next section.

Example 1: HF Buffer

In this example we will continue to use the hydrofluoric acid buffer. We will discuss the process for preparing a buffer of HF at a pH of 3.0. We can use the Henderson-Hasselbalch approximation to calculate the necessary ratio of F^- and HF.

$$pH = pKa + \log \frac{[Base]}{[Acid]} \tag{18.3.1}$$

$$3.0 = 3.18 + \log \frac{[Base]}{[Acid]} \tag{18.3.2}$$

$$\log \frac{[Base]}{[Acid]} = -0.18 \tag{18.3.3}$$

$$\frac{[Base]}{[Acid]} = 10^{-0.18} \tag{18.3.4}$$

$$\frac{[Base]}{[Acid]} = 0.66 \tag{18.3.5}$$

This is simply the ratio of the concentrations of conjugate base and conjugate acid we will need in our solution. However, what if we have 100 ml of 1 M HF and we want to prepare a buffer using NaF? How much Sodium Fluoride would we need to add in order to create a buffer at said pH (3.0)?

We know from our Henderson-Hasselbalch calculation that the ratio of our base/acid should be equal to 0.66. From a table of molar masses, such as a periodic table, we can calculate the molar mass of NaF to be equal to 41.99 g/mol. HF is a weak acid with a $K_a = 6.6 \times 10^{-4}$ and the concentration of HF is given above as 1 M. Using this information, we can calculate the amount of F^- we need to add.

The dissociation reaction is:

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons F^-_{(aq)} + H_3O^+_{(aq)} \tag{18.3.6}$$

We could use ICE tables to calculate the concentration of F^- from HF dissociation, but, since K_a is so small, we can approximate that virtually all of the HF will remain undissociated, so the amount of F^- in the solution from HF dissociation will be negligible. Thus, the [HF] is about 1 M and the [F^-] is close to 0. This will be especially true once we have added more F^-, the addition of which will even further suppress the dissociation of HF.

We want the ratio of Base/Acid to be 0.66, so we will need [Base]/1M = 0.66. Thus, [F^-] should be about 0.66 M. For 100 mL of solution, then, we will want to add 0.066 moles (0.1 L x 0.66 M) of F^-. Since we are adding NaF as our source of F^-, and since NaF completely dissociates in water, we need 0.066 moles of NaF. Thus, 0.066 moles x 41.99 g/mol = 2.767 g.

Note that, since the conjugate acid and the conjugate base are both mixed into the same volume of solution in the buffer, the ratio of "Base/Acid" is the same whether we use a ratio of the "concentration of base over concentration of acid," OR a ratio of "moles of base over moles of acid." The pH of the solution does not, it turns out, depend on the volume! (This is only true so long as the solution does not get so dilute that the autoionization of water becomes an important source of H^+ or OH^-. Such dilute solutions are rarely used as buffers, however.)

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1. Brown, et al. Chemistry:The Central Science. 11th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2008.
2. Chang, Raymond. General Chemistry:The Essential Concepts. 3rd ed. New York: Mcgraw Hill, 2003
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Outside Links

- Urbansky, Edward T.; Schock, Michael R. "Understanding, Deriving, and Computing Buffer Capacity." *J. Chem. Educ.* **2000** *1640.*.

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18.4: Titrations and pH 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 18.4.1a 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 18.4.1b. 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.

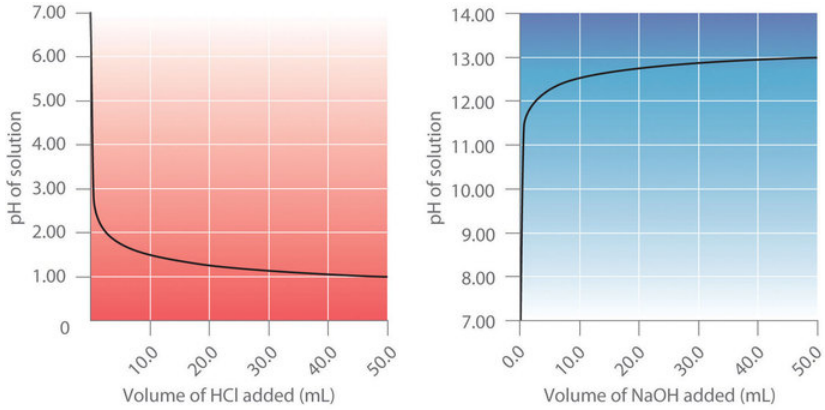


Figure 18.4.1: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 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 18.4.2a):

$$OH^- + H^+ \rightleftharpoons H_2O.$$

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:

$$\begin{aligned} moles\ of\ base &= (volume)_b(molarity)_b V_b M_b = moles\ of\ acid \\ &= (volume)_a(molarity)_a = V_a M_a \end{aligned} \tag{18.4.1}$$

If 0.20 M NaOH is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL$$

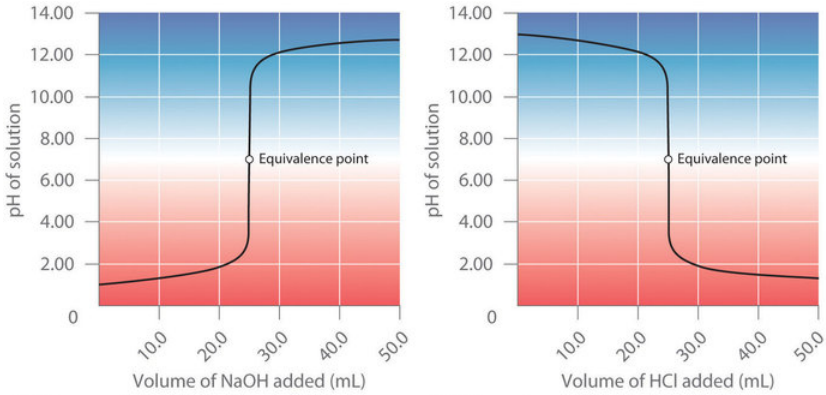


Figure 18.4.2: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M NaOH is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly 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 18.4.2*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 18.4.2*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 18.4.1: 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 H^+ and 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 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 H^+ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of OH^- to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess 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 H^+ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{-4}\ M$$

Hence,

$$pH \approx -\log[H^+] = -\log(3 \times 10^{-4}) = 3.5$$

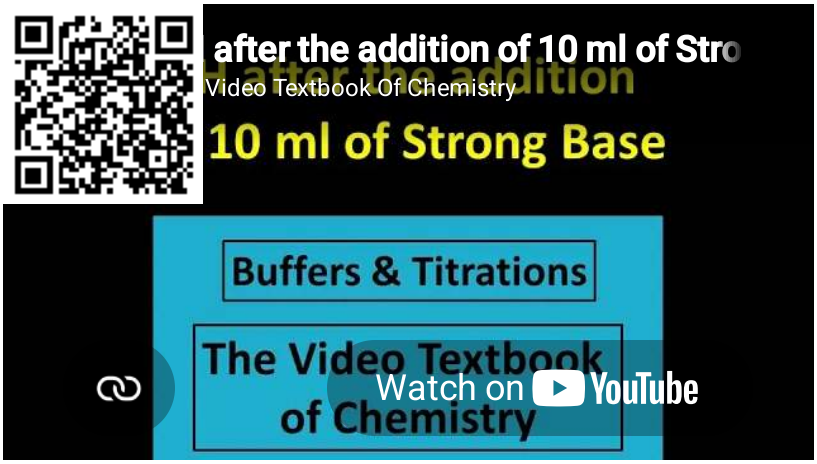
This is significantly less than the pH of 7.00 for a neutral solution.

? Exercise 18.4.1

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 $NaOH$.

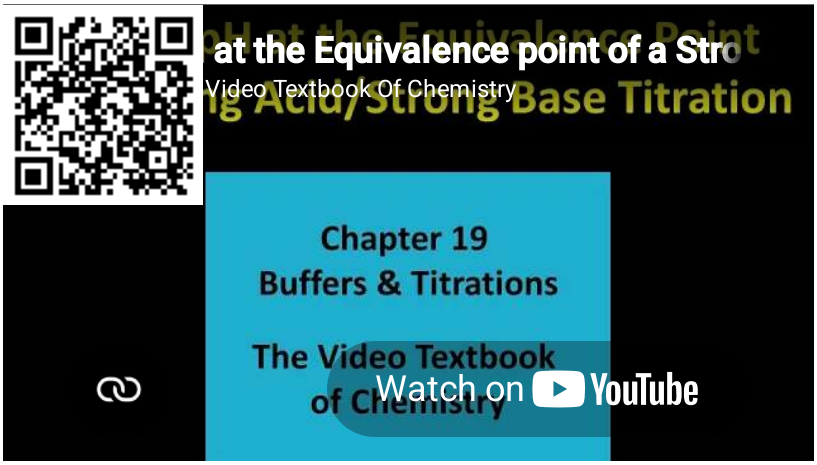
Answer

11.6



pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)



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, $[H^+]$ 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, [\(H^+] is less than [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 18.4.3a 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 18.4.2. 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.

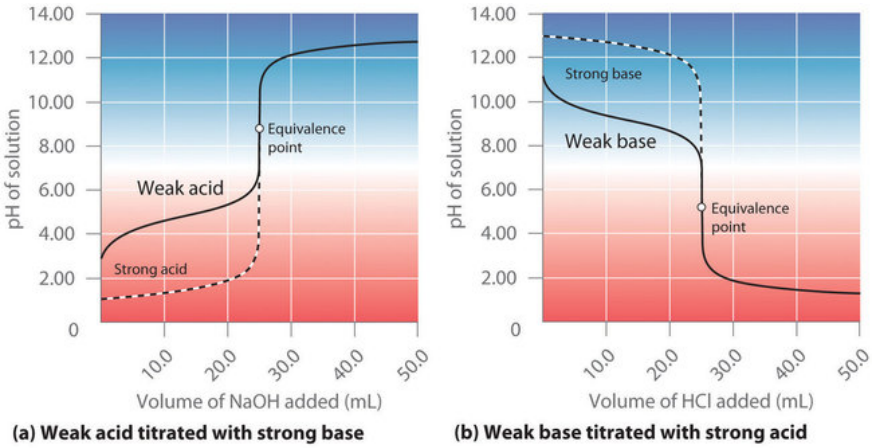


Figure 18.4.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more 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 18.4.3a 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 18.4.2 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 $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H\,(aq) \rightleftharpoons H^+\,(aq) + CH_3CO_2{}^-$$

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

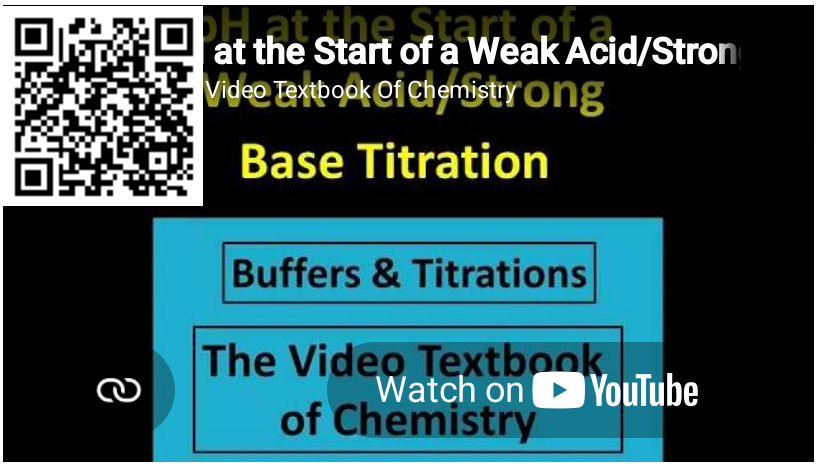
In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

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:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$



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 18.4.3). 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:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{18.4.2}$$

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 $[H^+]$ 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 CH_3CO_2H in the original solution and the amount of OH^- in the NaOH solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}\ (0.100\ mmol(CH_3CO_2H)/\cancel{mL}) = 5.00\ mmol(CH_3CO_2H)$$

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:

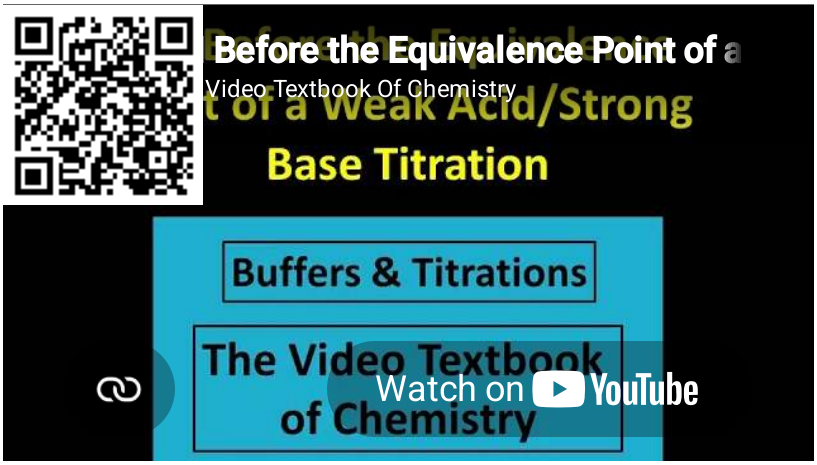
$$K_a = \frac{[CH_3CO_2^-]\,[H^+]}{[CH_3CO_2H]}$$

$$[H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{(1.72 \times 10^{-5})\,(7.27 \times 10^{-2}\ M)}{(1.82 \times 10^{-2})} = 6.95 \times 10^{-5}\ M$$

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 18.4.3*a*, 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 18.4.2, we calculate another point for constructing the titration curve of acetic acid.



pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example 18.4.2

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 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:

$$25.00 \text{ mL}(0.200 \text{ mmol OH}-\text{mL}=5.00 \text{ mmol } OH-$$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

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	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
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:

$$[CH_3CO_2] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)$$

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{18.4.3}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[OH^-]$ 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

	$[CH_3CO_2^-]$	$[CH_3CO_2H]$	$[OH^-]$
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 18.4.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} \tag{18.4.4}$$

Substituting the expressions for the final values from the ICE table into Equation 18.4.4 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 18.4.3a). 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 OH^-.

? Exercise 18.4.2

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

9.23

As shown in part (b) in Figure 18.4.3, 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 18.4.4 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.

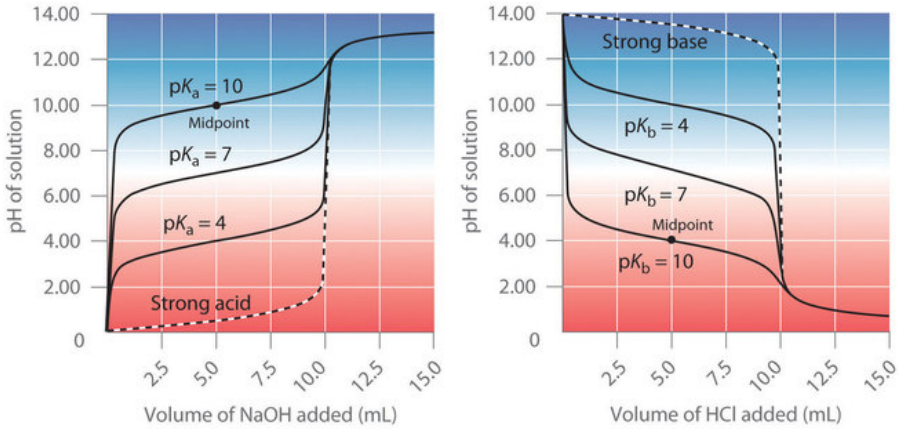


Figure 18.4.4: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added 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 18.4.4*a* and 18.4.4*b* 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

$$pK_a = pH \tag{18.4.5}$$

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 18.4.4 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 18.4.5 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.

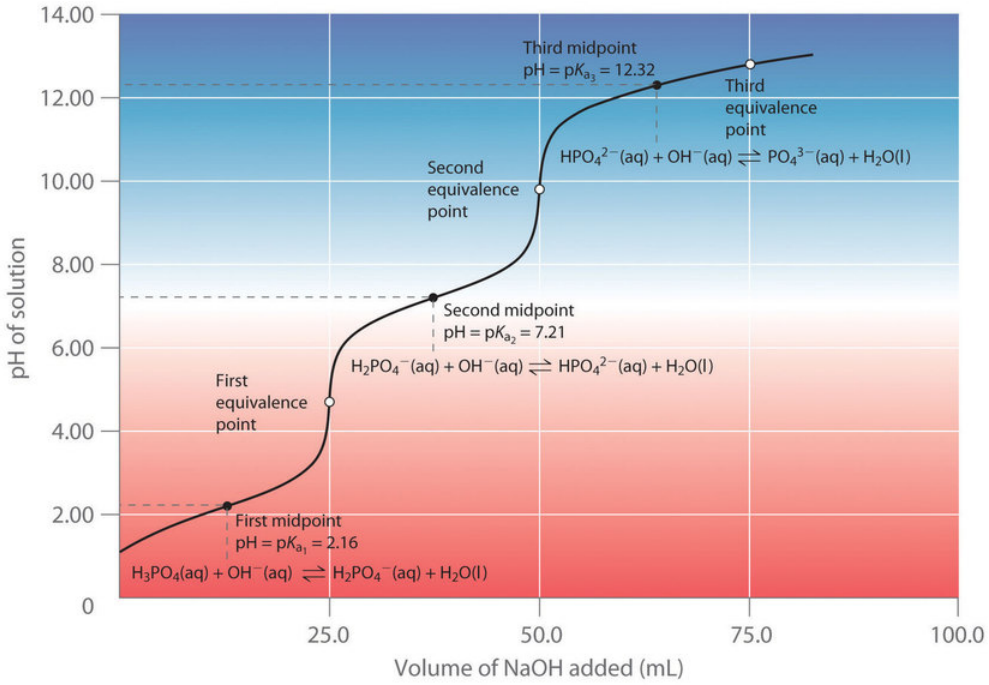
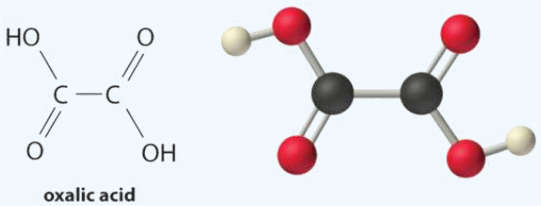


Figure 18.4.5: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^-$ 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 18.4.5. 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 18.4.3

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 (HO_2CCO_2H), a diprotic acid (abbreviated as 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 ($O_2CCO_2^{2-}$, abbreviated ox^{2-}).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as 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 $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 18.4.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$[ox^{2-}] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{[ox^{2-}]\,[H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$[H^+] = \frac{K_{a2}\,[Hox^-]}{[ox^{2-}]} = \frac{\left(1.6 \times 10^{-4}\right)\left(2.32 \times 10^{-2}\right)}{\left(9.68 \times 10^{-3}\right)} = 3.7 \times 10^{-4}\ M$$

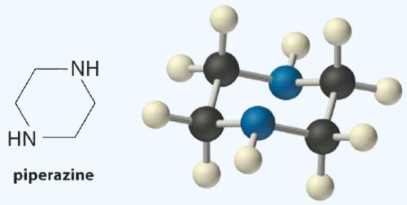
So

$$pH = -\log\left[H^+\right] = -\log\left(3.7 \times 10^{-4}\right) = 3.43$$

This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

? Exercise 18.4.3: 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.



Answer

pH=4.9

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:

$$\mathrm{HIn\,(aq)} \rightleftharpoons \mathrm{H^+\,(aq) + In^-\,(aq)}$$

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:

$$K_{In} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \tag{18.4.6}$$

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 18.4.6). 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 18.4.6: 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 18.4.7 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

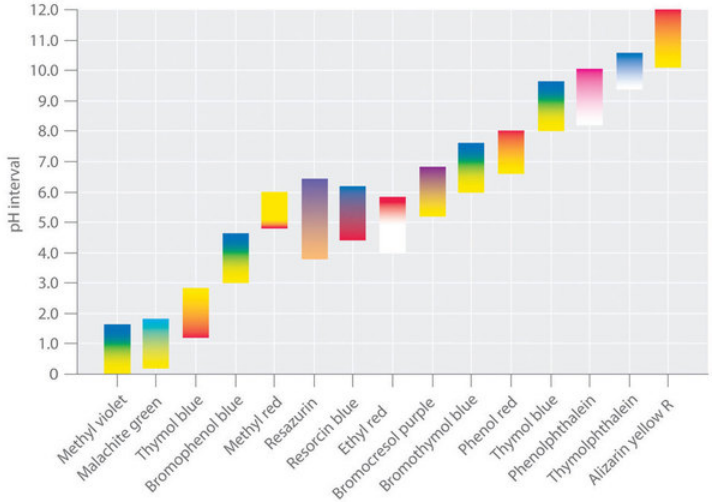


Figure 18.4.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

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 18.4.8. 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.

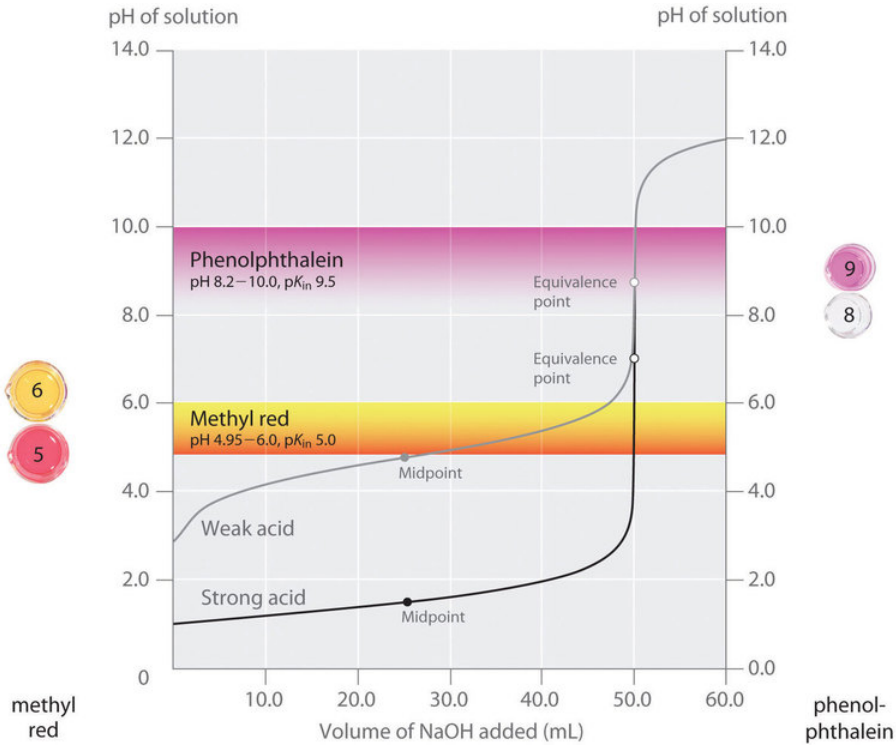


Figure 18.4.8: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

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 18.4.9).

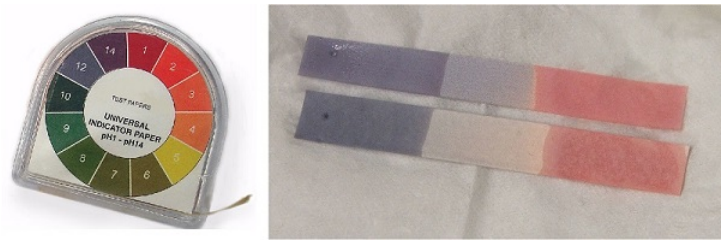
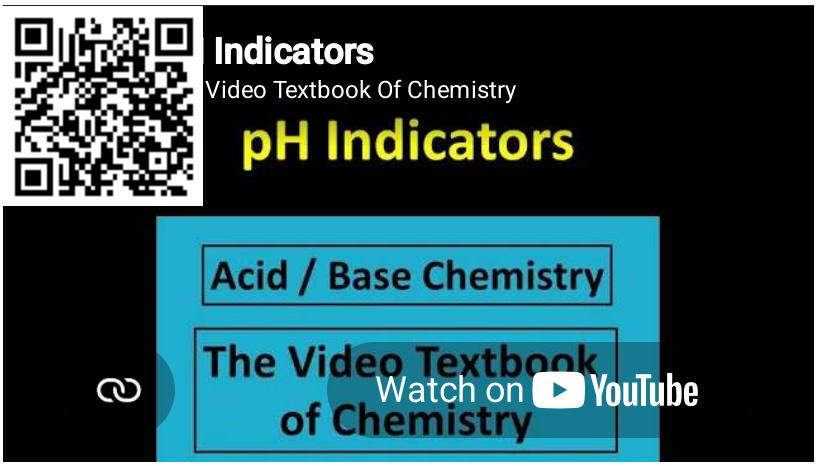


Figure 18.4.9: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)



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.

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18.5: Solubility Equilibria and the Solubility Product Constant

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{18.5.1}$$

As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca}^{2+}]^3[\mathrm{PO}_4^{3-}]^2}{[\mathrm{Ca}_3(\mathrm{PO}_4)_2]} \tag{18.5.2}$$

$$[\mathrm{Ca}_3(\mathrm{PO}_4)_2]K = K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}]^3[\mathrm{PO}_4^{3-}]^2 \tag{18.5.3}$$

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 18.5.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 18.5.2 and 18.5.3, changes in pH can affect the solubility of a compound as discussed later.

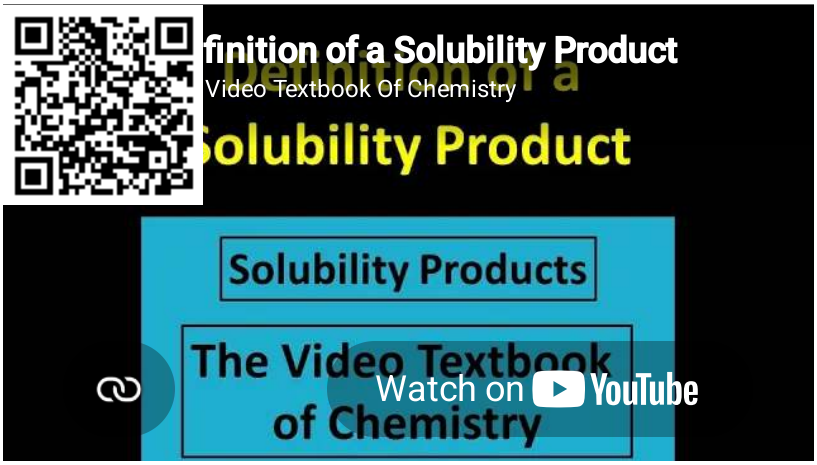
> *As with any K, the concentration of a pure solid does not appear explicitly in K_{sp}.*

Table 18.5.1: Solubility Products for Selected Ionic Substances at 25°C

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Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2 \cdot 3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}		**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}		$Ag_2C_2O_4$	white	5.40×10^{-12}
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.



Definition of a Solubility Product: Definition of a Solubility Product(opens in new window) [youtu.be]

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)\cdot H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 18.5.1

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}.

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:

$$Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^{-}O_2CCO_2^{-}(aq) + H_2O(l) \quad K_{sp} = [Ca^{2+}][ox^{2-}]$$

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:

$$\frac{7.36 \times 10^{-4}\ \text{g}}{146.1\ \text{g/mol}} = 5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2\cdot)\text{H}_2\text{O}}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right) = 5.04 \times 10^{-5}\ \text{mol/L} = 5.04 \times 10^{-5}\ \text{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04 × 10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

? Exercise 18.5.1: Calcite

One crystalline form of calcium carbonate ($CaCO_3$) is "calcite", found as both a mineral and a structural material in many organisms. Calcite is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. from Wikipedia

The solubility of calcite in water is 0.67 mg/100 mL. Calcite its K_{sp}.

Answer

4.5 × 10^{-9}

> *The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.*



Finding Ksp from Ion Concentrations: Finding Ksp from Ion Concentrations(opens in new window) [youtu.be]

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 18.5.1. 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 18.5.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.

B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 18.5.2) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Solutions to Example 17.4.2

	Ca3(PO4)2	[Ca2+]	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 \quad (18.5.4)$$

$$2.07 \times 10^{-33} = 108x^5 \quad (18.5.5)$$

$$1.92 \times 10^{-35} = x^5 \quad (18.5.6)$$

$$1.14 \times 10^{-7}\ \text{M} = x \quad (18.5.7)$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is 2*x* and 3*x*, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$$

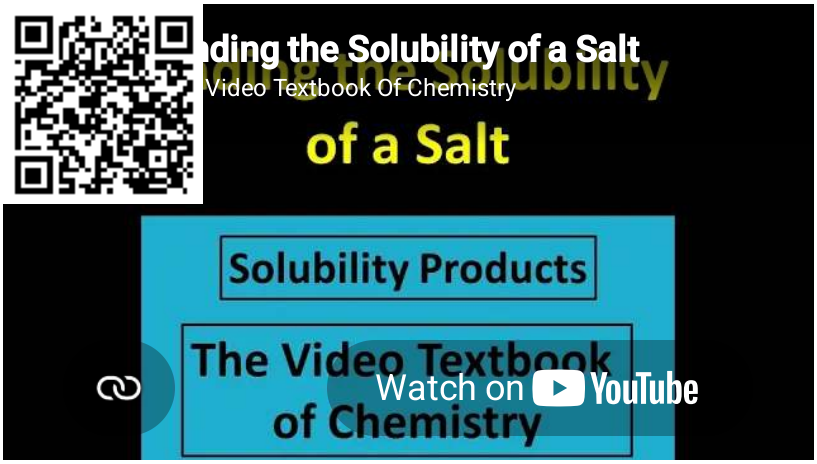
? Exercise 18.5.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer

a. 1.28×10^{-4} M
b. 3.54 mg



Finding the Solubility of a Salt: Finding the Solubility of a Salt (opens in new window) [youtu.be]

The Ion Product

The **ion product (*Q*)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

> *The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.*

As summarized in Figure 18.5.1, 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.

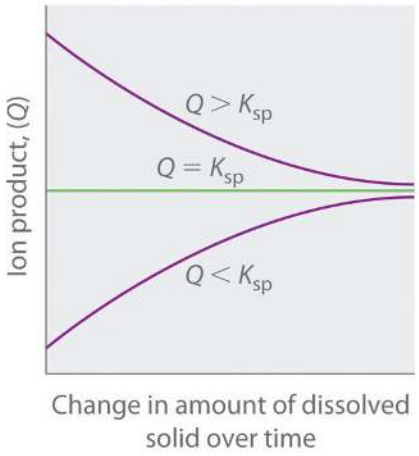


Figure 18.5.1: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

Graph of ion product against change in amount of dissolved solid over time. The purple curves are when Q is greater or less than Ksp. The green line is when Q is equal to Ksp.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 18.5.3

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:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$$

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 18.5.3

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

yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)



Determining if a Precipitate forms (The Ion Product): Determining if a Precipitate forms (The Ion Product)(opens in new window) [youtu.be]

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of

$Ca_3(PO_4)_2$ in water contains $3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7}\ M\ Ca^{2+}$ and $2 \times (1.14 \times 10^{-7}\ M) = 2.28 \times 10^{-7}\ M\ PO_4^{3-}$, according to the stoichiometry shown in Equation 18.5.1 (neglecting hydrolysis to form HPO_4^{2-} as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 18.5.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

> *The common ion effect usually **decreases** the solubility of a sparingly soluble salt.*

Example 18.5.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.

B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ is once again $+3x$, and the change in $[PO_4^{3-}]$ is $+2x$. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Solutions to Example 17.4.4

	Ca3(PO4)2	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07{\times}10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x << 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16}\ M \end{aligned}$$

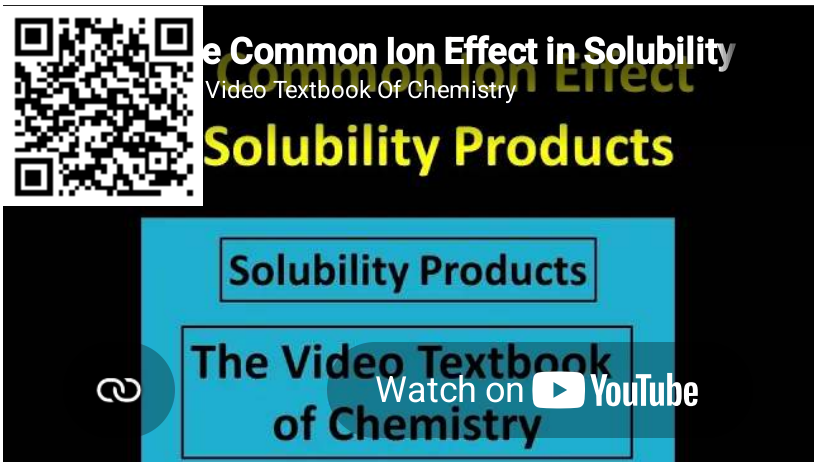
This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 18.5.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise 18.5.4

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

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



The Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products(opens in new window) [youtu.be]

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions. In contrast, the ion product (Q) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

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18.6: 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 Ba^{2+}:

$$BaCrO_4(s) \rightarrow Ba^{2+}(aq) + CrO_4{}^{2-}(aq)$$

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 $BaCrO_4$ to be much less soluble, and it will precipitate before any $SrCrO_4$ precipitates. If chromate concentration is maintained less than $1.2 \times 10^{-4} M$, then all Sr^{2+} ions will remain in the solution.

Discussion

In reality, controling the increase of $[CrO_4{}^{2-}]$ 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 $BaCrO_4$. Calculate $[Ba^{2+}]$ when the first trace of $SrCrO_4$ precipitate starts to form in a solution that contains 0.30 M each of Ba^{2+} and Sr^{2+} ions.

Solution

From the solution given in Example 18.6.1, $[CrO_4{}^{2-}] = 3.6 \times 10^{-4}\ M$ when $SrCrO_4$ starts to form. At this concentration, the $[Ba^{2+}]$ is estimated at $3.6 \times 10^{-4} = 1.2 \times 10^{-10}$.

The K_{sp} of $BaCrO_4$.

Thus,

$$[Ba^{2+}] = 3.33 \times 10^{-7}\ M$$

Very small indeed, compared to 0.30. In the fresh precipitate of $SrCrO_4$, the molar ratio of $SrCrO_4$ to $BaCrO_4$ is

$$\frac{0.30}{3.33 \times 10^{-7}} = 9.0 \times 10^{5}.$$

Hence, the amount of 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

$$[CrO_4{}^{2-}] = 3.6 \times 10^{-4} M.$$

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

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.

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}

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^+?



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: 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.

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 18.7.1. 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 18.7.1: 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 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:

$$Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)} \quad K_1 \tag{18.7.1}$$

$$[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)} \quad K_2 \tag{18.7.2}$$

$$[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)} \quad K_3 \tag{18.7.3}$$

$$[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \quad K_4 \tag{18.7.4}$$

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.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{18.7.5}$$

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:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{18.7.6}$$

> *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 $K_f = 2.1 \times 10^{13}$, 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 18.7.1.

Table 18.7.1: Common Complex Ions

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from Lange's Handbook of Chemistry, 15th ed. (1999).

Example 18.7.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6\,H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

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 18.7.5 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 18.7.6) 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 18.7.5. 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:

$$12.5 \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65 \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M \tag{18.7.7}$$

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.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
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 18.7.6) and assuming that $x << 0.0846$, which allows us to remove x from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13}$$

$$x = 2.1 \times 10^{-14}$$

The value of x indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

? Exercise 18.7.1

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.

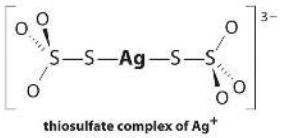
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Br^{-}_{(aq)} \tag{18.7.8}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25°C \tag{18.7.9}$$

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:

$$Ag^{+}_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{18.7.10}$$

with

$$K_f = 2.9 \times 10^{13} \tag{18.7.11}$$

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:

$$\text{AgBr(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Br}^-\text{(aq)} \quad K_{\text{sp}} = 5.35 \times 10^{-13} \tag{18.7.12}$$

$$\text{Ag}^+\text{(aq)} + 2\text{S}_2\text{O}_3^{2-}\text{(aq)} \rightleftharpoons [\text{Ag(S}_2\text{O}_3)_2]^{3-}\text{(aq)} \quad K_{\text{f}} = 2.9 \times 10^{13} \tag{18.7.13}$$

$$\text{AgBr(s)} + 2\text{S}_2\text{O}_3^{2-}\text{(aq)} \rightleftharpoons [\text{Ag(S}_2\text{O}_3)_2]^{3-}\text{(aq)} + \text{Br}^-\text{(aq)} \quad K = K_{\text{sp}}K_{\text{f}} = 15 \tag{18.7.14}$$

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 18.7.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let x equal the solubility of AgCl, then at equilibrium [Ag+] = $[Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77 \times 10^{-10}$$

$$x = 1.33 \times 10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77 \times 10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.77 \times 10^{-10} \tag{18.7.15}$$

$$Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^- \quad K_f = 1.1 \times 10^5 \tag{18.7.16}$$

$$AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^- \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{18.7.17}$$

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 18.7.2

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

$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

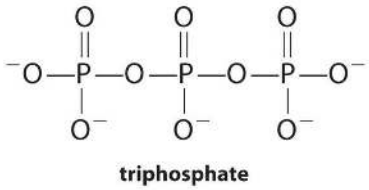
Answer a

1.9×10^{-10} M

Answer a

1.4 M

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

$$Ca^{2+}(aq) + O_3POPO_4^{4-}(aq) \rightleftharpoons [Ca(O_3POPO_3)]^{2-}(aq) \tag{18.7.18}$$

with

$$K_f = 4 \times 10^4 \tag{18.7.19}$$

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.

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.

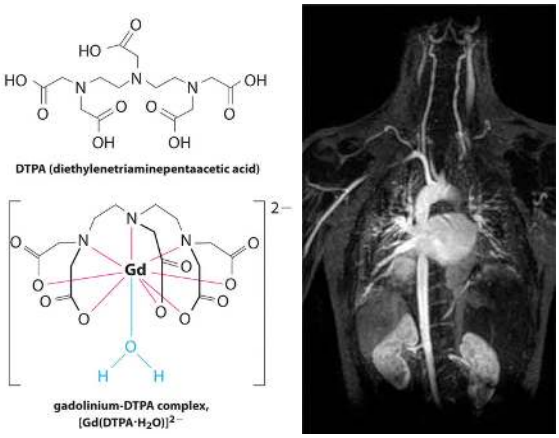


Figure 18.7.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

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 18.7.2). 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.

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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CHAPTER OVERVIEW

19: Free Energy and Thermodynamics

19.1: Energy Spreads Out
19.2: Spontaneous and Nonspontaneous Processes
19.3: Entropy and the Second Law of Thermodynamics
19.4: Predicting Entropy and Entropy Changes for Chemical Reactions
19.5: Heat Transfer and Changes in the Entropy of the Surroundings
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19.1: Energy Spreads Out



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19.2: Spontaneous and Nonspontaneous Processes

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 19.2.1).

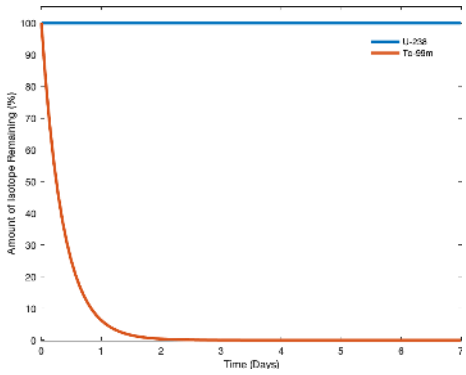


Figure 19.2.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

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 19.2.2).

$$\mathrm{C(s,\,diamond)} \longrightarrow \mathrm{C(s,\,graphite)} \tag{19.2.1}$$

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.

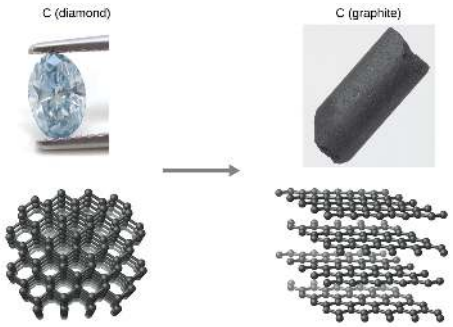


Figure 19.2.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures 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 19.2.3). 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.

$$w = -P\Delta V \tag{19.2.2}$$

$$= 0 \;\; (\mathrm{P} = 0 \text{ in a vaccum}) \tag{19.2.3}$$

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.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \qquad (19.2.4)$$

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).

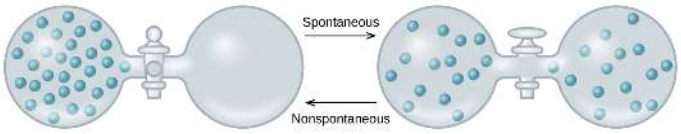


Figure 19.2.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.
When the valve is closed, all of the gas molecules accumlating 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 19.2.4). 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.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \qquad (19.2.5)$$

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 19.2.4: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 19.2.1: 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 19.2.5:(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 19.2.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

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.

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

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19.3: Entropy and the Second Law of Thermodynamics

Learning Objectives

- To understand the relationship between internal energy and entropy.

The first law of thermodynamics governs changes in the state function we have called internal energy (U). Changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure 19.3.1.

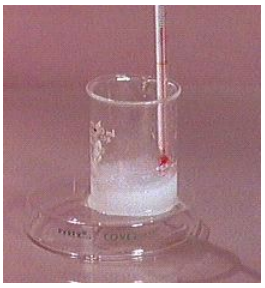


Figure 19.3.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called **entropy (S)**, a thermodynamic property of all substances that is proportional to their degree of "disorder". In Chapter 13, we introduced the concept of entropy in relation to solution formation. Here we further explore the nature of this state function and define it mathematically.

Entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure 19.3.2. In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately 10^{68} different ways they might be arranged, which corresponds to 10^{68} different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

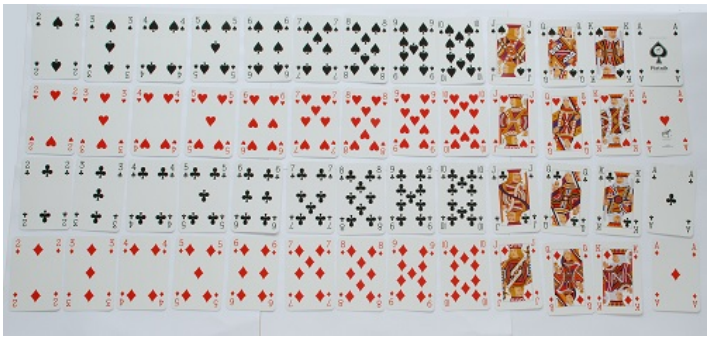


Figure 19.3.2: Illustrating Low- and High-Entropy States with a Deck of Playing Cards. An new, unshuffled deck has only a single arrangement, so there is only one microstate. In contrast, a randomly shuffled deck can have any one of approximately 10^{68} different arrangements, which correspond to 10^{68} different microstates. (CC BY-3.0 ; Trainler).

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure 19.3.3). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure 19.3.3, arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter, with half the gas molecules in each bulb, is the most probable arrangement. The others are not impossible but simply less likely.

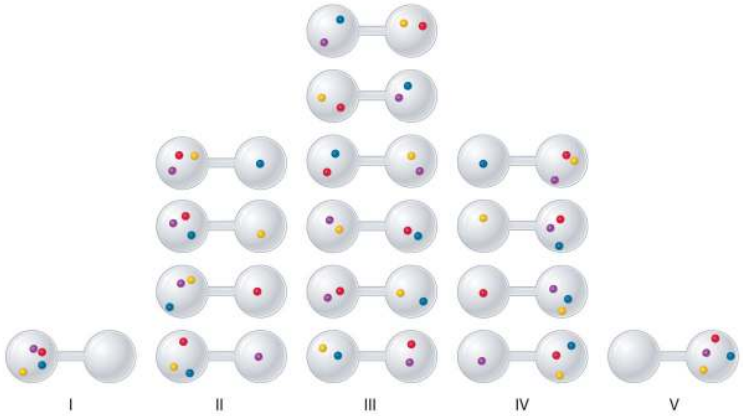


Figure 19.3.3: The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume

There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is so improbable that it is likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Instead of four molecules of gas, let's now consider 1 L of an ideal gas at standard temperature and pressure (STP), which contains 2.69×10^{22} molecules (6.022×10^{23} molecules/22.4 L). If we allow the sample of gas to expand into a second 1 L container, the probability of finding all 2.69×10^{22} molecules in one container and none in the other at any given time is extremely small, approximately $\frac{2}{2.69 \times 10^{22}}$. The probability of such an occurrence is effectively zero. Although nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are many equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

> Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 19.3.4, 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 $\Delta S_{soln} > 0$.

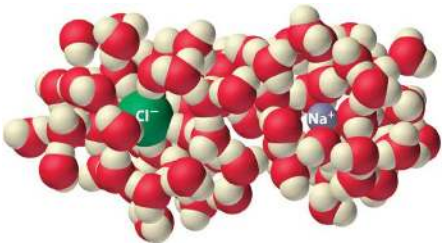


Figure 19.3.4: The Effect of Solution Formation on Entropy

Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

✔ Example 19.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.
b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

? Exercise 19.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer a

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

Answer a

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

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{19.3.1}$$

> Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{\text{rev}} = T\Delta S \quad \text{and} \quad \Delta S = \frac{q_{\text{rev}}}{T} \tag{19.3.2}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation 19.3.1 as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{19.3.3}$$

$$= T\Delta S - P\Delta V \tag{19.3.4}$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 19.3.2 and Equation 19.3.4, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 19.3.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, $\Delta V > 0$, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0.$$

According to Equation 19.3.4, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore $\Delta S_{sys} = +q_{rev}/T$, and the entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}.$$

The corresponding change in entropy of the universe is then as follows:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= \frac{q_{\text{rev}}}{T} + \left(-\frac{q_{\text{rev}}}{T}\right) \\ &= 0\end{aligned}$$

Thus no change in ΔS_{univ} has occurred.

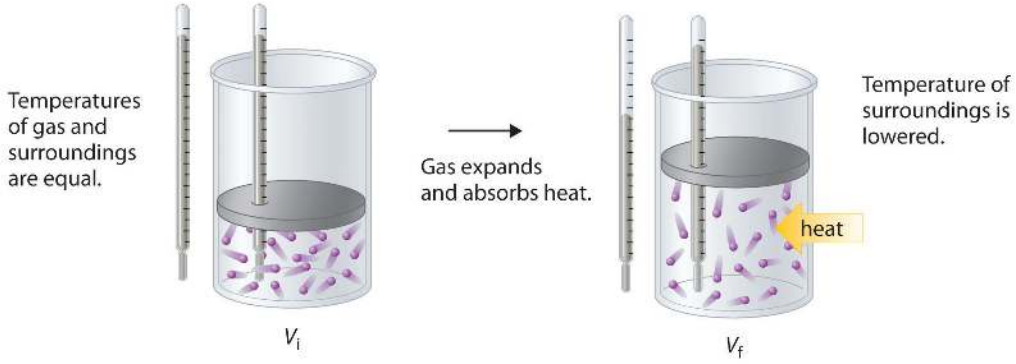


Figure 19.3.5: Expansion of Gas at Constant Temperature

Temperatures of gas and surroundings are equal. Then the gas expands and absorbs heat. Temperature of the surroundings is then lowered.

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 19.3.6. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 19.3.2, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T}$$

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

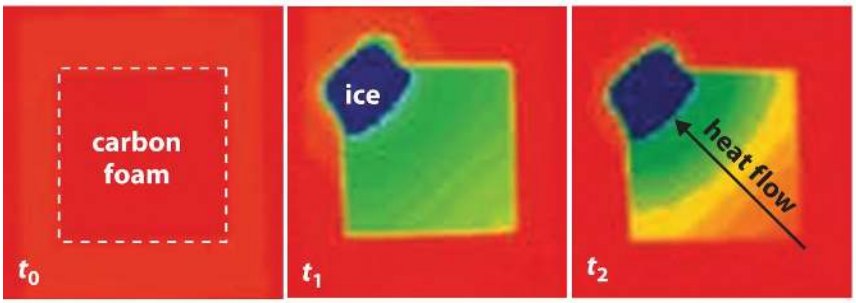


Figure 19.3.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

In this case, ΔS_{fus} = (6.01 kJ/mol)/(273 K) = 22.0 J/(mol•K) = ΔS_{sys}. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so $\Delta S_{surr} = q_{rev}/T$ = −(6.01 kJ/mol)/(273 K) = −22.0 J/(mol•K). Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 22.0 \text{ J/(mol•K)} - 22.0 \text{ J/(mol•K)} = 0$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat (q > 0), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat (q < 0), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} = \frac{q}{T_{\text{cold}}} + \left(-\frac{q}{T_{\text{hot}}}\right) \tag{19.3.5}$$

The numerators on the right side of Equation 19.3.5 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} is negative will not occur as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 19.3.7).



Figure 19.3.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

Example 19.3.2: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to have plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and may have disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with ΔH = −2.1 kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 19.3.2 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 19.3.2 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where q_{rev} = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \text{J/(mol}\cdot\text{K)}$$

b. The fact that ΔS < 0 means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.



Video 19.3.1**:** *Time lapse tin pest reaction.*

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C)

? Exercise 19.3.2

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with ΔH = 0.401 kJ/mol at 1 atm.

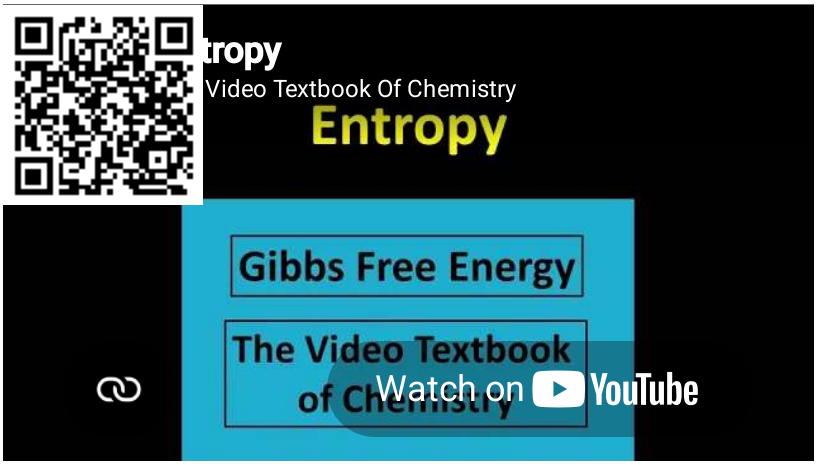
a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a

1.09 J/(mol•K)

Answer b

S_α



Entropy: Entropy(opens in new window) [youtu.be]

Summary

For a given system, the greater the number of microstates, the higher the entropy. During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

A measure of the disorder of a system is its entropy (S), a state function whose value increases with an increase in the number of available microstates. A reversible process is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

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19.4: Predicting Entropy and Entropy Changes for Chemical Reactions

Learning Objectives

- To calculate entropy changes for a chemical reaction

We have seen that the energy given off (or absorbed) by a reaction, and monitored by noting the change in temperature of the surroundings, can be used to determine the enthalpy of a reaction (e.g. by using a calorimeter). Tragically, there is no comparable easy way to experimentally measure the change in entropy for a reaction. Suppose we know that energy is going into a system (or coming out of it), and yet we do not observe any change in temperature. What is going on in such a situation? Changes in internal energy, that are not accompanied by a temperature change, might reflect changes in the entropy of the system.

For example, consider water at °0C at 1 atm pressure

- This is the temperature and pressure condition where liquid and solid phases of water are in equilibrium (also known as the melting point of ice)

$$\mathrm{H_2O\,(s)} \rightarrow \mathrm{H_2O\,(l)} \tag{19.4.1}$$

- At such a temperature and pressure we have a situation (by definition) where we have some ice and some liquid water
- If a small amount of energy is input into the system the equilibrium will shift slightly to the right (i.e. in favor of the liquid state)
- Likewise if a small amount of energy is withdrawn from the system, the equilibrium will shift to the left (more ice)

> *However, in both of the above situations, the energy change is not accompanied by a change in temperature (the temperature will not change until we no longer have an equilibrium condition; i.e. all the ice has melted or all the liquid has frozen)*

Since the quantitative term that relates the amount of heat energy input vs. the rise in temperature is the heat capacity, it would seem that in some way, information about the heat capacity (and how it changes with temperature) would allow us to determine the entropy change in a system. In fact, values for the "standard molar entropy" of a substance have units of J/mol K, the same units as for molar heat capacity.

Standard Molar Entropy, S^0

The entropy of a substance has an absolute value of 0 entropy at 0 K.

- **Standard molar entropies** are listed for a reference temperature (like 298 K) and 1 atm pressure (i.e. the entropy of a pure substance at 298 K and 1 atm pressure). A table of standard molar entropies at 0K would be pretty useless because it would be 0 for every substance (duh!) Standard molar entropy values are listed for a variety of substances in Table T2.
- When comparing standard molar entropies for a substance that is either a solid, liquid or gas at 298 K and 1 atm pressure, the gas will have more entropy than the liquid, and the liquid will have more entropy than the solid
- Unlike *enthalpies of formation*, standard molar entropies of elements are not 0.

The entropy change in a chemical reaction is given by the sum of the entropies of the products minus the sum of the entropies of the reactants. As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation (the *n*, and *m*, terms below are there to indicate that the coefficients must be accounted for):

$$\Delta S^0 = \sum_n nS^0(products) - \sum_m mS^0(reactants)$$

Example 19.4.1: Haber Process

Calculate the change in entropy associated with the Haber process for the production of ammonia from nitrogen and hydrogen gas.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightleftharpoons \mathrm{2\,NH_3\,(g)}$$

At 298K as a standard temperature:

- $S^0(NH_3)$ = 192.5 J/mol K
- $S^0(H_2)$ = 130.6 J/mol K
- $S^0(N_2)$ = 191.5 J/mol K

Solution

From the balanced equation we can write the equation for ΔS^0 (the change in the standard molar entropy for the reaction):

$\Delta S^0 = 2*S^0(NH_3) - [S^0(N_2) + (3*S^0(H_2))]$

$\Delta S^0 = 2*192.5 - [191.5 + (3*130.6)]$

$\Delta S^0 = -198.3$ J/mol K

It would appear that the process results in a ***decrease*** in entropy - i.e. a decrease in disorder. This is expected because we are decreasing the number of gas molecules. In other words the $N_2(g)$ used to float around independently of the H_2 gas molecules. After the reaction, the two are bonded together and can't float around freely from one another. (I guess you can consider marriage as a negative entropy process!)

To calculate ΔS° for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 19.4.2 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

ΔS° for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate ΔH°.

Example 19.4.2: Combustion of Octane

Use the data in Table T2 to calculate ΔS° for the combustion reaction of liquid isooctane with O_2(g) to give CO_2(g) and H_2O(g) at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table T2. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$\mathrm{C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \;\rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(g)}$$

We calculate ΔS° for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})\\ &= [8S^\circ(\mathrm{CO_2}) + 9S^\circ(\mathrm{H_2O})] - [S^\circ(\mathrm{C_8H_{18}}) + \frac{25}{2}S^\circ(\mathrm{O_2})]\\ &= \{[8\text{ mol }\mathrm{CO_2} \times 213.8\text{ J/(mol}\cdot\text{K)}] + [9\text{ mol }\mathrm{H_2O} \times 188.8\text{ J/(mol}\cdot\text{K)}]\}\\ &\quad - \left\{[1\text{ mol }\mathrm{C_8H_{18}} \times 329.3\text{ J/(mol}\cdot\text{K)}] + \left[\frac{25}{2}\text{ mol }\mathrm{O_2} \times 205.2\text{ J/(mol}\cdot\text{K)}\right]\right\}\\ &= 515.3\text{ J/K}\end{aligned}$$

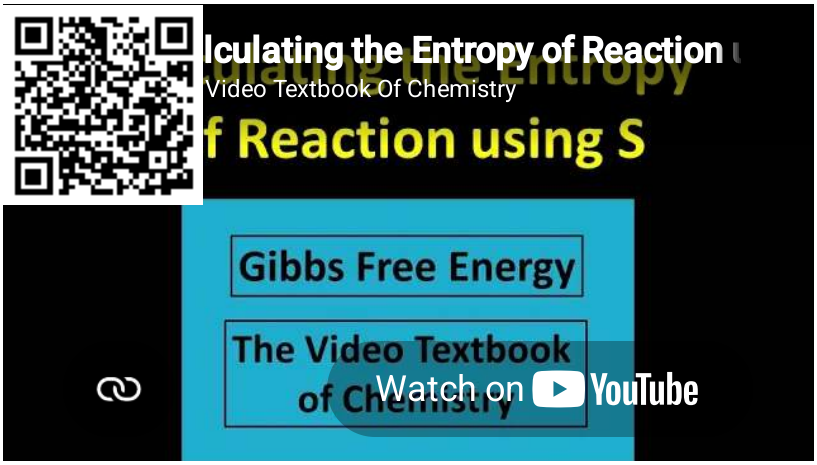
ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 19.4.2

Use the data in Table T2 to calculate ΔS° for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer

−361.1 J/K



Calculating the Entropy of Reaction using S: Calculating the Entropy of Reaction using S(opens in new window) [youtu.be]

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19.5: Heat Transfer and Changes in the Entropy of the Surroundings



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19.6: Gibbs Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{19.6.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled “On the Equilibrium of Heterogeneous Substances” was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{19.6.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 19.6.2 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{19.6.3}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{19.6.4}$$

$$= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \tag{19.6.5}$$

Multiplying both sides of the inequality by −T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0$$

which is equal to ΔG (Equation 19.6.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 19.6.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 19.6.3), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1091\ \text{J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\text{ J} - [(363.15\text{ K})(108.96\text{ J/K})] \\ &= 1088\text{ J}\end{aligned}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ\text{C}} = 1090\text{ J} = -\Delta G_{90^\circ\text{C}}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 19.6.2), setting $\Delta G = 0$, and solving for T,

$$0\text{ J} = 40{,}657\text{ J} - T(108.96\text{ J/K})$$
$$T = 373.15\text{ K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 19.6.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

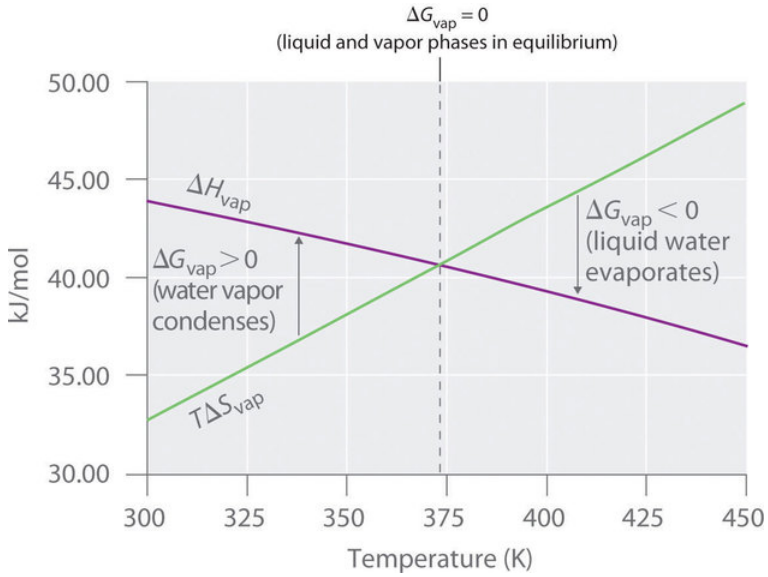
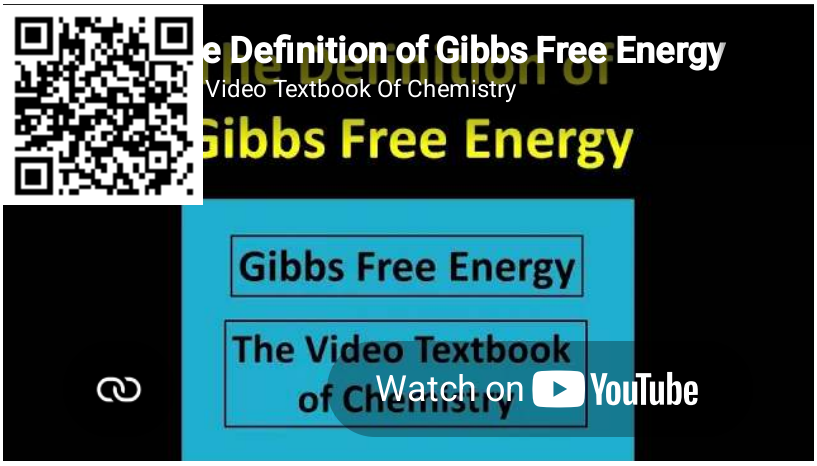


Figure 19.6.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

Graph of kilojoule per mole against temperature. The purple line is the delta H vaporization. the green line is the T delta S vaporization.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate

as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.



The Definition of Gibbs Free Energy: The Definition of Gibbs Free Energy (opens in new window) [youtu.be]

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 19.6.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{19.6.6}$$

This equation tells us that when energy is released during an exothermic process (ΔH < 0), such as during the combustion of a fuel, some of that energy can be used to do work (ΔG < 0), while some is used to increase the entropy of the universe (TΔS > 0). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 19.6.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 19.6.1: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 19.6.7:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19.6.7}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

Example 19.6.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 19.6.7, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH^o, ΔS^o, and T. We are given ΔH^o, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\text{ mol }\mathrm{H_2O_2} \times 109.6\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol }\mathrm{H_2} \times 130.7\text{ J/(mol}\cdot\text{K)}] + [1\text{ mol }\mathrm{O_2} \times 205.2\text{ J/(mol}\cdot\text{K)}]\} \\ &= -226.3\text{ J/K (per mole of }\mathrm{H_2O_2})\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS^o is very negative for this reaction.

B Substituting the appropriate quantities into Equation 19.6.7,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\text{ kJ/mol} - (298.15\text{ K})[-226.3\text{ J/(mol}\cdot\text{K)} \times 1\text{ kJ/1000 J}] \\ &= -187.78\text{ kJ/mol} + 67.47\text{ kJ/mol} \\ &= -120.31\text{ kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS^o and ΔH^o for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH^o and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS^o term and for the energy needed to break bonds in the reactants.

? Exercise 19.6.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

Hint

At 25°C, the standard enthalpy change (ΔH^o) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

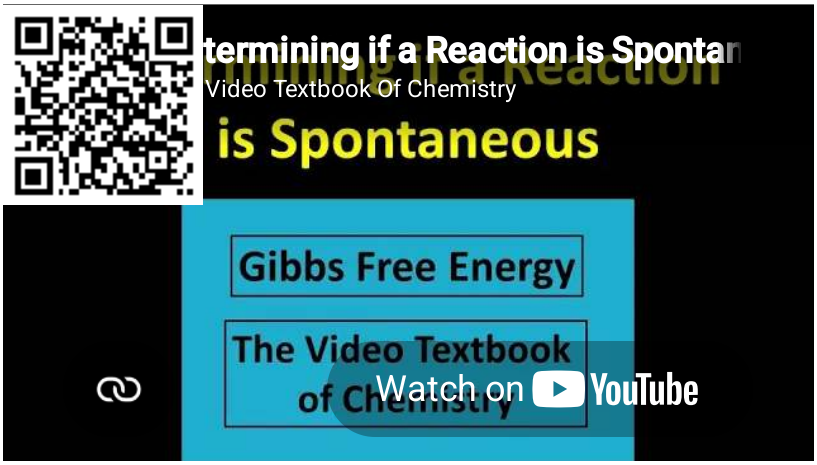
- S°(N_2H_4) = 121.2 J/(mol•K),
- S°(N_2) = 191.6 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Answer

149.5 kJ/mol

no, not spontaneous

Video Solution



Determining if a Reaction is Spontaneous: Determining if a Reaction is Spontaneous(opens in new window) [youtu.be] (opens in new window)

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG_f°)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G_f^\circ = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{19.6.8}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o(products) - \sum n\Delta_f^o(reactants) \tag{19.6.9}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 19.6.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- 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:

$$C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \;\rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(l)$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, $\Delta G^\circ_f\,(O_2)$ is zero. Using the "products minus reactants" rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G^\circ_f(CO_2) + 9\Delta G^\circ_f(H_2O)] - \left[1\Delta G^\circ_f(C_8H_{18}) + \frac{25}{2}\Delta G^\circ_f(O_2)\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } C_8H_{18})\end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

? Exercise 19.6.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

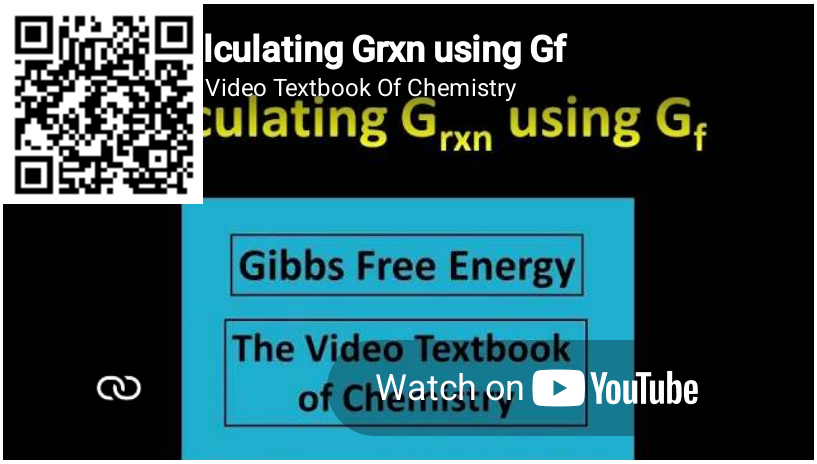
- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Video Solution



Calculating Grxn using Gf: Calculating Grxn using Gf(opens in new window) [youtu.be]

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do

not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

> In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 19.6.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- $\Delta H^\circ_f\,(NH_3)$ = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 19.6.7 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 19.6.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 19.6.7, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{rxn} &= 2S^\circ(NH_3) - [S^\circ(N_2) + 3S^\circ(H_2)]\\ &= [2\text{ mol } NH_3 \times 192.8\text{ J/(mol}\cdot\text{K)}]\\ &\quad - \{[1\text{ mol } N_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol } H_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\}\\ &= -198.1\text{ J/K (per mole of } N_2)\end{aligned} \tag{19.6.10}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of $\Delta H^\circ_f\,(NH_3)$ is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{rxn} &= 2\Delta H^\circ_f(NH_3) - [\Delta H^\circ_f(N_2) + 3\Delta H^\circ_f(H_2)]\\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})]\\ &= -91.8\text{ kJ(per mole of } N_2)\end{aligned}$$

B Inserting the appropriate values into Equation 19.6.7

$$\begin{aligned}\Delta G^\circ_{rxn} = \Delta H^\circ - T\Delta S^\circ &= (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ/1000 J})\\ &= -32.7\text{ kJ (per mole of } N_2)\end{aligned}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 19.6.2:

$$\begin{aligned}\Delta G_{300°C} &= \Delta H_{300°C} - (573\text{ K})(\Delta S_{300°C})\\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ\\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ/1000 J})\\ &= 21.7\text{ kJ (per mole of } N_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice,

it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

? Exercise 19.6.3

Calculate

a. $\Delta G°$ and
b. $\Delta G_{750°C}$

for the following reaction

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- 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

Answer b

33.8 kJ/mol of O_2

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 19.6.7, as illustrated in Example 19.6.4.

✓ Example 19.6.4

As you saw in Example 19.6.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 19.6.7 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 19.6.7 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

? Exercise 19.6.4

As you found in the exercise in Example 19.6.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Video Solution

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

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19.7: Free Energy Changes in Chemical Reactions- Calculating

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{19.7.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled “On the Equilibrium of Heterogeneous Substances” was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{19.7.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 19.7.2 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{19.7.3}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{19.7.4}$$

$$= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \tag{19.7.5}$$

Multiplying both sides of the inequality by −T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0$$

which is equal to ΔG (Equation 19.7.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 19.7.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 19.7.3), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1091\ \text{J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ C} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= 1088\ \text{J}\end{aligned}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ C} = 1090\ \text{J} = -\Delta G_{90^\circ C}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 19.7.2), setting $\Delta G = 0$, and solving for T,

$$0\ \text{J} = 40{,}657\ \text{J} - T(108.96\ \text{J/K})$$
$$T = 373.15\ \text{K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 19.7.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

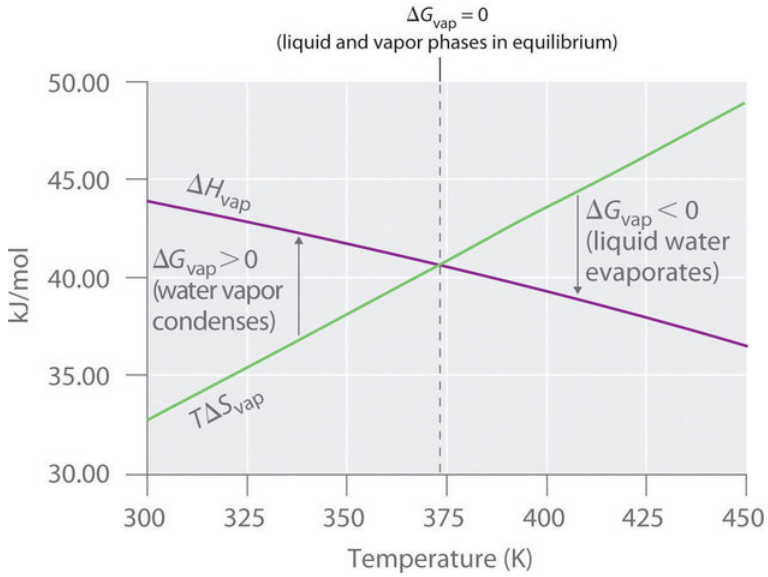
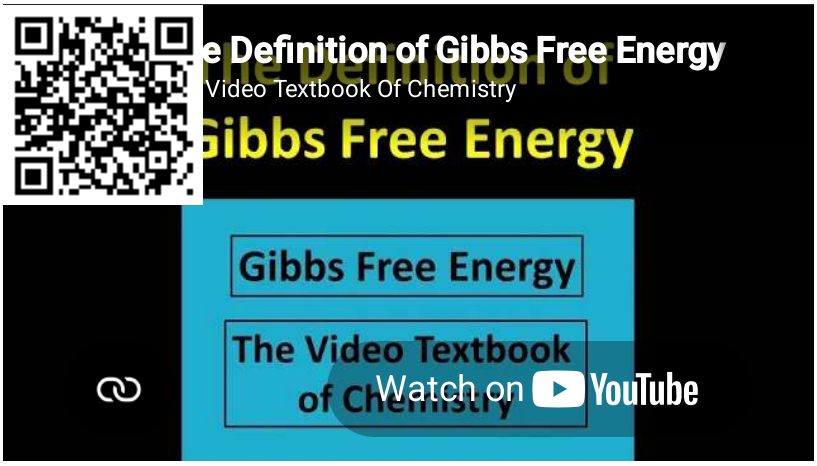


Figure 19.7.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

Graph of kilojoule per mole against temperature. The purple line is the delta H vaporization. the green line is the T delta S vaporization.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate

as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.



The Definition of Gibbs Free Energy: The Definition of Gibbs Free Energy (opens in new window) [youtu.be]

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 19.7.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{19.7.6}$$

This equation tells us that when energy is released during an exothermic process (ΔH < 0), such as during the combustion of a fuel, some of that energy can be used to do work (ΔG < 0), while some is used to increase the entropy of the universe (TΔS > 0). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 19.7.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 19.7.1: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 19.7.7:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19.7.7}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

Example 19.7.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 19.7.7, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH^o, ΔS^o, and T. We are given ΔH^o, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\text{ mol }\mathrm{H_2O_2} \times 109.6\text{ J/(mol}\cdot\mathrm{K})] \\ &\quad - \{[1\text{ mol }\mathrm{H_2} \times 130.7\text{ J/(mol}\cdot\mathrm{K})] + [1\text{ mol }\mathrm{O_2} \times 205.2\text{ J/(mol}\cdot\mathrm{K})]\} \\ &= -226.3\text{ J/K (per mole of }\mathrm{H_2O_2})\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS^o is very negative for this reaction.

B Substituting the appropriate quantities into Equation 19.7.7,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\text{ kJ/mol} - (298.15\text{ K})[-226.3\text{ J/(mol}\cdot\mathrm{K}) \times 1\text{ kJ/1000 J}] \\ &= -187.78\text{ kJ/mol} + 67.47\text{ kJ/mol} \\ &= -120.31\text{ kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS^o and ΔH^o for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH^o and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS^o term and for the energy needed to break bonds in the reactants.

? Exercise 19.7.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

Hint

At 25°C, the standard enthalpy change (ΔH^o) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

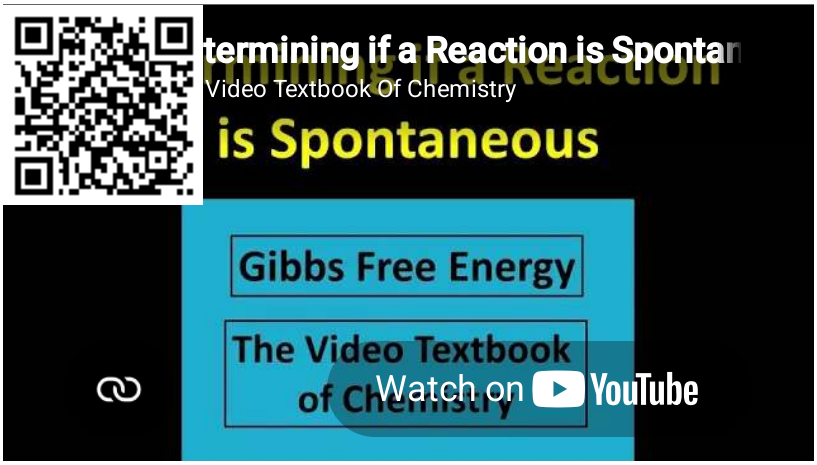
- S°(N_2H_4) = 121.2 J/(mol•K),
- S°(N_2) = 191.6 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Answer

149.5 kJ/mol

no, not spontaneous

Video Solution



Determining if a Reaction is Spontaneous: Determining if a Reaction is Spontaneous(opens in new window) [youtu.be] (opens in new window)

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG_f°)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G_f^\circ = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{19.7.8}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o(products) - \sum n\Delta_f^o(reactants) \tag{19.7.9}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 19.7.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- 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:

$$C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \;\rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(l)$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, $\Delta G^\circ_f\,(O_2)$ is zero. Using the "products minus reactants" rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G^\circ_f(CO_2) + 9\Delta G^\circ_f(H_2O)] - \left[1\Delta G^\circ_f(C_8H_{18}) + \frac{25}{2}\Delta G^\circ_f(O_2)\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } C_8H_{18})\end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

? Exercise 19.7.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

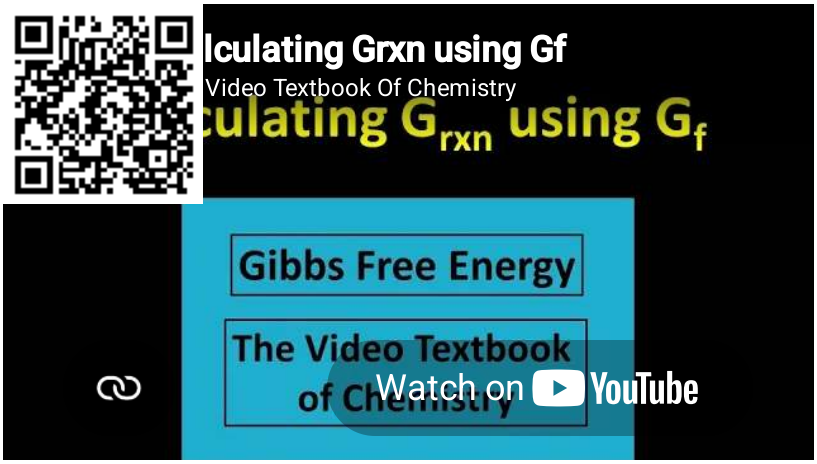
- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Video Solution



Calculating Grxn using Gf: Calculating Grxn using Gf(opens in new window) [youtu.be]

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do

not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

> In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 19.7.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- $\Delta H^\circ_f\,(NH_3)$ = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 19.7.7 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 19.7.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 19.7.7, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{rxn} &= 2S^\circ(NH_3) - [S^\circ(N_2) + 3S^\circ(H_2)]\\ &= [2\text{ mol } NH_3 \times 192.8\text{ J/(mol}\cdot\text{K)}]\\ &\quad - \{[1\text{ mol } N_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol } H_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\}\\ &= -198.1\text{ J/K (per mole of } N_2)\end{aligned} \tag{19.7.10}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of $\Delta H^\circ_f\,(NH_3)$ is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{rxn} &= 2\Delta H^\circ_f(NH_3) - [\Delta H^\circ_f(N_2) + 3\Delta H^\circ_f(H_2)]\\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})]\\ &= -91.8\text{ kJ(per mole of } N_2)\end{aligned}$$

B Inserting the appropriate values into Equation 19.7.7

$$\begin{aligned}\Delta G^\circ_{rxn} = \Delta H^\circ - T\Delta S^\circ &= (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ/1000 J})\\ &= -32.7\text{ kJ (per mole of } N_2)\end{aligned}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 19.7.2:

$$\begin{aligned}\Delta G_{300°C} &= \Delta H_{300°C} - (573\text{ K})(\Delta S_{300°C})\\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ\\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ/1000 J})\\ &= 21.7\text{ kJ (per mole of } N_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice,

it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

Exercise 19.7.3

Calculate

a. $\Delta G°$ and
b. $\Delta G_{750°C}$

for the following reaction

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- 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

Answer b

33.8 kJ/mol of O_2

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 19.7.7, as illustrated in Example 19.7.4.

Example 19.7.4

As you saw in Example 19.7.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 19.7.7 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 19.7.3, 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 19.7.7 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

? Exercise 19.7.4

As you found in the exercise in Example 19.7.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Video Solution

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

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19.8: Free Energy Changes for Nonstandard States - The Relationship between and

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 19.8.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 19.8.1: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K
*Spontaneous in the reverse direction.		

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG^o) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH^o and ΔS^o determine the magnitude and sign of ΔG^o and also because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG^o and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follows (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{19.8.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 19.8.1 simplifies to

$$\Delta G = V\Delta P \tag{19.8.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 19.8.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{19.8.3}$$

$$= nRT\frac{\Delta P}{P} \tag{19.8.4}$$

$$= nRT\ln\left(\frac{P_f}{P_i}\right) \tag{19.8.5}$$

If the initial state is the standard state with $P_i = 1\ atm$, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT \ln P$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{19.8.6}$$

As you will soon discover, Equation 19.8.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{19.8.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{19.8.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{19.8.9}$$

Substituting Equation 19.8.6 for each term into Equation 19.8.9,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_{\mathrm{C}}^c P_{\mathrm{D}}^d}{P_{\mathrm{A}}^a P_{\mathrm{B}}^b} \right) \tag{19.8.10}$$

$$= \Delta G^\circ + RT \ln Q \tag{19.8.11}$$

where ΔG^o indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^o + RT \ln K_p \tag{19.8.12}$$

$$\Delta G^o = -RT \ln K_p \tag{19.8.13}$$

If the products and reactants are in their standard states and $\Delta G^o < 0$, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if $\Delta G^o > 0$, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If $\Delta G^o = 0$, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

Example 19.8.1

ΔG^o is −32.7 kJ/mol of N_2 for the reaction

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- $P_{\mathrm{N_2}}$ = 2.00 atm,
- $P_{\mathrm{H_2}}$ = 7.00 atm,
- $P_{\mathrm{NH_3}}$ = 0.021 atm, and
- $T = 100^oC$.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

A. Using the values given and Equation 19.8.11, calculate Q.
B. Determine if Q is >, <, or = to K
C. Substitute the values of ΔG^o and Q into Equation 19.8.11 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG^o and ΔG under nonstandard conditions is given in Equation 19.8.11. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{\mathrm{NH_3}}^2}{P_{\mathrm{N_2}} P_{\mathrm{H_2}}^3}$$
$$= \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Because ΔG^o is −, K must be a number greater than 1

C Substituting the values of ΔG^o and Q into Equation 19.8.11,

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \ln(6.4 \times 10^{-7})\right]$$
$$= -32.7 \text{ kJ} + (-44 \text{ kJ})$$
$$= -77 \text{ kJ/mol of } \mathrm{N_2}$$

Because $\Delta G < 0$ and $Q < K$ (because $Q < 1$), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

? Exercise 19.8.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and $P_{NO_2} = 1.00 \times 10^{-4} atm$. The value of ΔG^o for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written. The reaction will proceed in the forward direction to reach equilibrium.

✔ Example 19.8.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG^o for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 19.8.1, ΔG^o, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG^o and T (in kelvin) into Equation 19.8.13 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 19.8.1, we used tabulated values of ΔG°_f to calculate ΔG^o for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 19.8.13,

$$\Delta G^\circ = -RT \ln K_\text{p}$$

$$\frac{-\Delta G^\circ}{RT} = \ln K_\text{p}$$

Inserting the value of ΔG^o 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 product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? Exercise 19.8.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG^o for this reaction is −70.5 kJ/mol of O_2.

Answer

2.3×10^{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. The numerical magnitude of K_p and K are related:

$$K_p = K(RT)^{\Delta n} \tag{19.8.14}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 19.8.13 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{19.8.15}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 19.8.15 for the difference between K_p and K.

Non-Ideal Behavior

Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

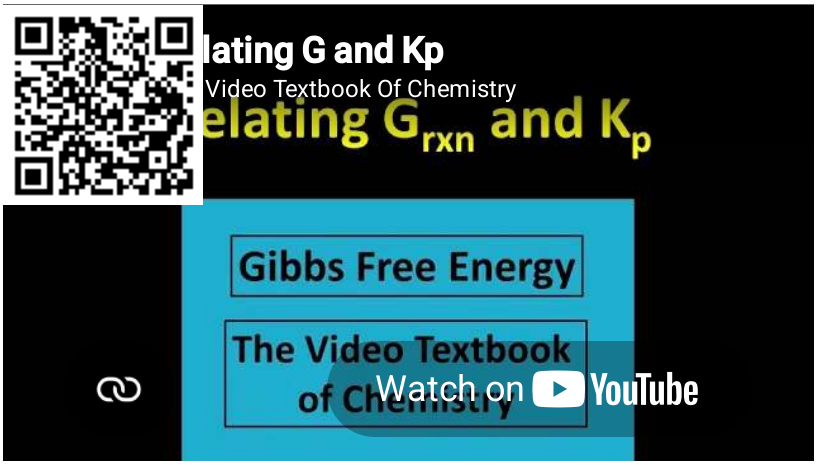
Combining Equation 19.8.15 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG^o influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19.8.16}$$

$$= -RT \ln K \tag{19.8.17}$$

Notice that K becomes larger as ΔS^o becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH^o decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.*



Relating Grxn and Kp: Relating Grxn and Kp(opens in new window) [youtu.be]

Temperature Dependence of the Equilibrium Constant

The fact that ΔG^o and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 19.8.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{19.8.18}$$

Assuming ΔH^o and ΔS^o are temperature independent, for an exothermic reaction ($\Delta H^o < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 19.8.18 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 19.8.18 also shows that the magnitude of ΔH^o dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS^o affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH^o for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS^o. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 19.8.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{19.8.19}$$

Thus calculating ΔH^o from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH^o and ΔS^o are independent of temperature.

Example 19.8.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 19.8.3. What is K_p at 500°C? (Use the data from Example 19.8.1.)

Given: balanced chemical equation, ΔH^{o}°, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 19.8.19 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH^{o} for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 19.8.19 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10}$$

$$K_2 = (5.4 \times 10^{5})(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}$$

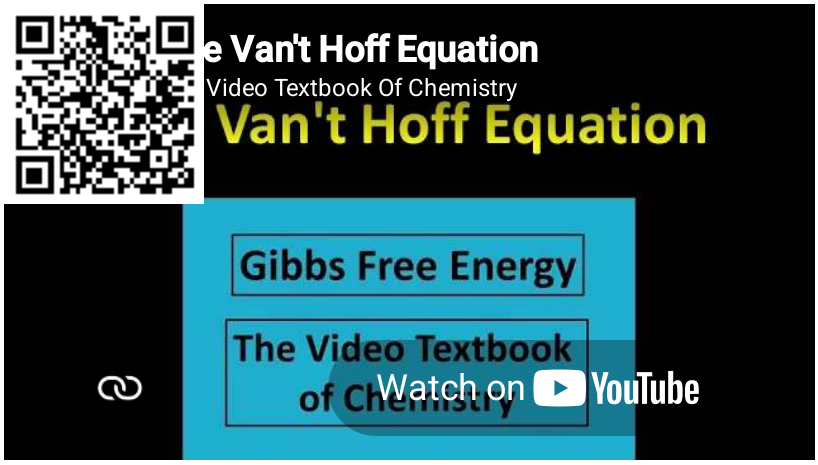
Thus at 500°C, the equilibrium strongly favors the reactants over the products.

? Exercise 19.8.4

In the exercise in Example 19.8.3, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH_f^{o} values in the exercise in Example 19.8.1 to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}



The Van't Hoff Equation: The Van't Hoff Equation (opens in new window) [youtu.be]

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G^{o} < 0$, then K > 1, and products are favored over reactants at equilibrium. Conversely, if $\Delta G^{o} > 0$, then K < 1, and reactants are favored over products at equilibrium. If

ΔG^o = 0, then K=1, and neither reactants nor products are favored at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

- Mike Blaber (Florida State University)
- Modified by Tom Neils (Grand Rapids Community College)

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19.9: Free Energy and Equilibrium- Relating to the Equilibrium Constant (K)

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 19.9.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 19.9.1: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K
*Spontaneous in the reverse direction.		

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG^o) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH^o and ΔS^o determine the magnitude and sign of ΔG^o and also because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG^o and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follows (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{19.9.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 19.9.1 simplifies to

$$\Delta G = V\Delta P \tag{19.9.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 19.9.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{19.9.3}$$

$$= nRT\frac{\Delta P}{P} \tag{19.9.4}$$

$$= nRT\ln\left(\frac{P_f}{P_i}\right) \tag{19.9.5}$$

If the initial state is the standard state with $P_i = 1\ atm$, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT \ln P$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{19.9.6}$$

As you will soon discover, Equation 19.9.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{19.9.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{19.9.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{19.9.9}$$

Substituting Equation 19.9.6 for each term into Equation 19.9.9,

$$\Delta G = [(cG_C^o + cRT \ln P_C) + (dG_D^o + dRT \ln P_D)] - [(aG_A^o + aRT \ln P_A) + (bG_B^o + bRT \ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_{\mathrm{C}}^c P_{\mathrm{D}}^d}{P_{\mathrm{A}}^a P_{\mathrm{B}}^b} \right) \tag{19.9.10}$$

$$= \Delta G^\circ + RT \ln Q \tag{19.9.11}$$

where ΔG^o indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^o + RT \ln K_p \tag{19.9.12}$$

$$\Delta G^o = -RT \ln K_p \tag{19.9.13}$$

If the products and reactants are in their standard states and $\Delta G^o < 0$, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if $\Delta G^o > 0$, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If $\Delta G^o = 0$, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

Example 19.9.1

ΔG^o is −32.7 kJ/mol of N_2 for the reaction

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- $P_{\mathrm{N_2}}$ = 2.00 atm,
- $P_{\mathrm{H_2}}$ = 7.00 atm,
- $P_{\mathrm{NH_3}}$ = 0.021 atm, and
- $T = 100^oC$.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

A. Using the values given and Equation 19.9.11, calculate Q.
B. Determine if Q is >, <, or = to K
C. Substitute the values of ΔG^o and Q into Equation 19.9.11 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG^o and ΔG under nonstandard conditions is given in Equation 19.9.11. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{\mathrm{NH_3}}^2}{P_{\mathrm{N_2}} P_{\mathrm{H_2}}^3}$$
$$= \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Because ΔG^o is −, K must be a number greater than 1

C Substituting the values of ΔG^o and Q into Equation 19.9.11,

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \ln(6.4 \times 10^{-7})\right]$$
$$= -32.7 \text{ kJ} + (-44 \text{ kJ})$$
$$= -77 \text{ kJ/mol of } \mathrm{N_2}$$

Because $\Delta G < 0$ and $Q < K$ (because $Q < 1$), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

? Exercise 19.9.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and $P_{NO_2} = 1.00 \times 10^{-4} atm$. The value of ΔG^o for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written. The reaction will proceed in the forward direction to reach equilibrium.

✔ Example 19.9.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG^o for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 19.9.1, ΔG^o, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG^o and T (in kelvin) into Equation 19.9.13 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 19.9.1, we used tabulated values of ΔG°_f to calculate ΔG^o for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 19.9.13,

$$\Delta G^\circ = -RT \ln K_\text{p}$$

$$\frac{-\Delta G^\circ}{RT} = \ln K_\text{p}$$

Inserting the value of ΔG^o 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 product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? Exercise 19.9.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG^o for this reaction is −70.5 kJ/mol of O_2.

Answer

2.3×10^{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. The numerical magnitude of K_p and K are related:

$$K_p = K(RT)^{\Delta n} \tag{19.9.14}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 19.9.13 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{19.9.15}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 19.9.15 for the difference between K_p and K.

Non-Ideal Behavior

Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

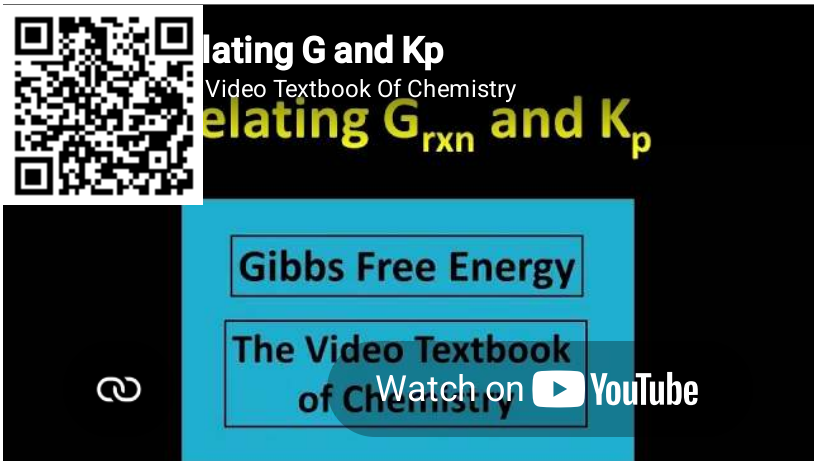
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$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19.9.16}$$

$$= -RT \ln K \tag{19.9.17}$$

Notice that K becomes larger as ΔS^o becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH^o decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.*



Relating Grxn and Kp: Relating Grxn and Kp(opens in new window) [youtu.be]

Temperature Dependence of the Equilibrium Constant

The fact that ΔG^o and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 19.9.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{19.9.18}$$

Assuming ΔH^o and ΔS^o are temperature independent, for an exothermic reaction ($\Delta H^o < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 19.9.18 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 19.9.18 also shows that the magnitude of ΔH^o dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS^o affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH^o for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS^o. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 19.9.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{19.9.19}$$

Thus calculating ΔH^o from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH^o and ΔS^o are independent of temperature.

Example 19.9.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 19.9.3. What is K_p at 500°C? (Use the data from Example 19.9.1.)

Given: balanced chemical equation, ΔH^{o}°, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 19.9.19 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH^{o} for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 19.9.19 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10}$$

$$K_2 = (5.4 \times 10^{5})(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}$$

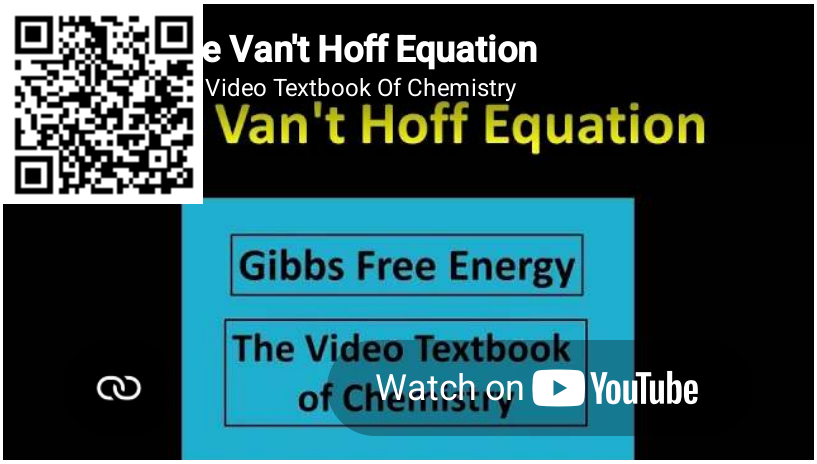
Thus at 500°C, the equilibrium strongly favors the reactants over the products.

? Exercise 19.9.4

In the exercise in Example 19.9.3, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH_f^{o} values in the exercise in Example 19.9.1 to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}



The Van't Hoff Equation: The Van't Hoff Equation (opens in new window) [youtu.be]

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G^{o} < 0$, then K > 1, and products are favored over reactants at equilibrium. Conversely, if $\Delta G^{o} > 0$, then K < 1, and reactants are favored over products at equilibrium. If

ΔG^o = 0, then K=1, and neither reactants nor products are favored at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

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CHAPTER OVERVIEW

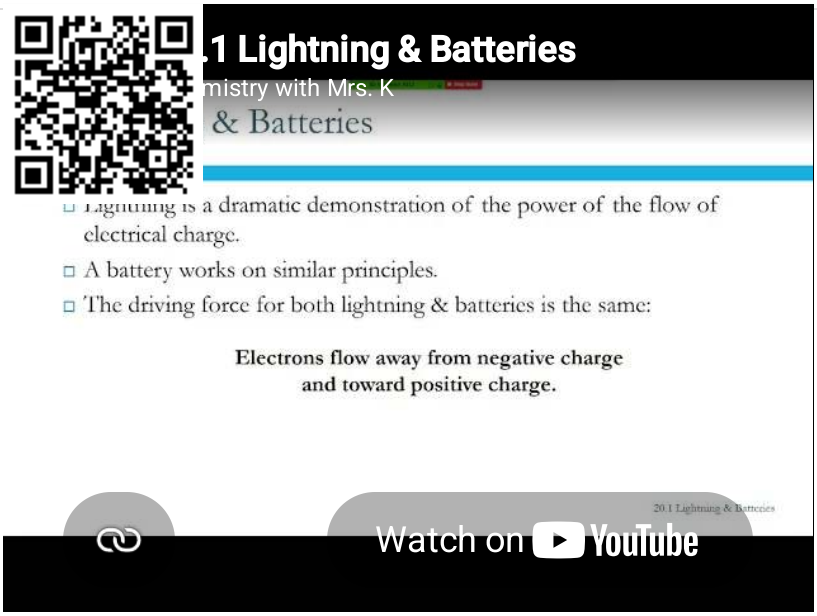
20: Electrochemistry

Topic hierarchy

20.1: Lightning and Batteries
20.2: Balancing Oxidation-Reduction Equations
20.3: Voltaic (or Galvanic) Cells- Generating Electricity from Spontaneous Chemical Reactions
20.4: Standard Reduction Potentials
20.5: Cell Potential, Gibbs Energy, and the Equilibrium Constant
20.6: Cell Potential and Concentration
20.7: Batteries- Using Chemistry to Generate Electricity
20.8: Electrolysis- Driving Non-spontaneous Chemical Reactions with Electricity
20.9: Corrosion- Undesirable Redox Reactions

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20.1: Lightning and Batteries



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20.2: Balancing Oxidation-Reduction Equations

Learning Objectives

- To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method.

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method, we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of $Cr^{2+}(aq)$ with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 20.2.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described previously (in red above each element):

$$\overset{+2}{\mathrm{Cr}}^{2+}(aq) + \overset{+4}{\mathrm{Mn}}\overset{-2}{\mathrm{O}}_2(aq) + \overset{+1}{\mathrm{H}}^{+}(aq) \rightarrow \overset{+3}{\mathrm{Cr}}^{3+}(aq) + \overset{+2}{\mathrm{Mn}}^{2+}(aq) + \overset{+1}{\mathrm{H}}_2\overset{-2}{\mathrm{O}}(l) \tag{20.2.1}$$

Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced (ignoring the oxygen and hydrogen atoms):

$$\mathrm{Cr}^{2+} + \mathrm{Mn}^{4+} \longrightarrow \mathrm{Cr}^{3+} + \mathrm{Mn}^{2+} \tag{20.2.2}$$

The oxidation can be written as

$$\underbrace{\mathrm{Cr}^{2+} \longrightarrow \mathrm{Cr}^{3+} + \mathrm{e}^-}_{\text{oxidation with 1 electron lost}} \tag{20.2.3}$$

and the reduction as

$$\underbrace{\mathrm{Mn}^{4+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Mn}^{2+}}_{\text{reduction with 2 electrons gained}} \tag{20.2.4}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation (Equation 20.2.3) by 2 to give

$$2\,\mathrm{Cr}^{2+} \longrightarrow 2\,\mathrm{Cr}^{3+} + 2\,\mathrm{e}^- \tag{20.2.5}$$

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction (Equation 20.2.4):

$$2\,\mathrm{Cr}^{2+} \rightarrow 2\,\mathrm{Cr}^{3+} + 2\,\mathrm{e}^-$$

$$\mathrm{Mn}^{4+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Mn}^{2+}$$

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:

$$2\,\mathrm{Cr}^{2+} \rightarrow 2\,\mathrm{Cr}^{3+} + \cancel{2\,\mathrm{e}^-}$$

$$\mathrm{Mn}^{4+} + \cancel{2\,\mathrm{e}^-} \rightarrow \mathrm{Mn}^{2+}$$

to result in the balanced redox reaction (metals only)

$$\mathrm{Mn^{4+} + 2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + Mn^{2+}} \tag{20.2.6}$$

now we can add the non-redox active atoms back into the equation (ignoring water and hydronium for now)

$$\mathrm{MnO_2\,(aq) + 2\,Cr^{2+}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq)} \tag{20.2.7}$$

> *In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.*

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of Equation 20.2.7 (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add $\mathrm{H^+}$ 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 $\mathrm{OH^-}$ as necessary to either side of the equation to balance the charges.

In this case, adding four $\mathrm{H^+}$ ions to the left side of Equation 20.2.7 to give

$$\mathrm{MnO_2\,(s) + 2\,Cr^{2+}\,(aq) + 4\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq)} \tag{20.2.8}$$

Although the charges are now balanced in Equation 20.2.8, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding $\mathrm{H_2O}$ as necessary to either side of the equation. Here, we need to add two $\mathrm{H_2O}$ molecules to the right side of Equation 20.2.8:

$$\mathrm{MnO_2\,(s) + 2\,Cr^{2+}\,(aq) + 4\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq) + 2\,H_2O\,(l)} \tag{20.2.9}$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced with respect to all atoms and charge. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized below and illustrated in Example 20.2.1 below.

Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding $\mathrm{H^+}$ or $\mathrm{OH^-}$ ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding $\mathrm{H_2O}$ molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

Example 20.2.1: Balancing in Acid Solutions

Arsenic acid ($\mathrm{H_3AsO_4}$) 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 ($\mathrm{AsH_3}$, a highly toxic and unstable gas) and $\mathrm{Zn^{2+}\,(aq)}$. Balance the equation for this reaction using oxidation states:

$$\mathrm{H_3AsO_4\,(aq) + Zn\,(s) \longrightarrow AsH_3\,(g) + Zn^{2+}\,(aq)}$$

Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given above for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

1. *Write a chemical equation showing the reactants and the products.* Because we are given this information, we can skip this step.
2. *Assign oxidation states and determine which atoms change oxidation state.* The oxidation state of arsenic in arsenic acid is +5, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$\overset{+5}{H_3As}O_4(aq) + \overset{0}{Zn}(s) \rightarrow \overset{-3}{As}H_3(g) + \overset{+2}{Zn^{2+}}(aq)$$

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:

$$\underbrace{\overset{+5}{As} + 8e^- \rightarrow \overset{-3}{As}}_{\text{Reduction with gain of 8 electrons}}$$

Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$\underbrace{\overset{0}{Zn} \rightarrow \overset{+2}{Zn^{2+}} + 2e^-}_{\text{Oxidation with loss of 2 electrons}}$$

4. *Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.* The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain

$$\overset{+5}{\mathrm{As}} + 8\,\mathrm{e^-} \rightarrow \overset{-3}{\mathrm{As}}$$
$$4\,\overset{0}{\mathrm{Zn}} \rightarrow 4\,\overset{+2}{\mathrm{Zn^{2+}}} + 8\,\mathrm{e^-}$$

5. *Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.* Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives
   - Reduction:

$$\mathrm{H_3AsO_4\,(aq) + 8\,e^-} \rightarrow \mathrm{AsH_3\,(g)}$$

   - Oxidation:

$$\mathrm{4\,Zn\,(s)} \longrightarrow \mathrm{4\,Zn^{2+}\,(aq) + 8\,e^-}$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$\mathrm{H_3AsO_4\,(aq) + 4\,Zn\,(s) + \cancel{8e^-} \rightarrow AsH_3\,(g) + 4\,Zn^{2+}\,(aq) + \cancel{8e^-}}$$

which then yields after canceling electrons

$$\mathrm{H_3AsO_4\,(aq) + 4\,Zn\,(s) \rightarrow AsH_3\,(g) + 4\,Zn^{2+}\,(aq)}$$

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:

$$\mathrm{H_3AsO_4\,(aq) + 4\,Zn\,(s) + 8\,H^+\,(aq) \rightarrow AsH_3\,(g) + 4\,Zn^{2+}\,(aq)}$$

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:

$$H_3AsO_4\,(aq) + 4\,Zn\,(s) + 8\,H^+\,(aq) \rightarrow AsH_3\,(g) + 4\,Zn^{2+}\,(aq) + 4\,H_2O\,(l)$$

Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:
   - Atoms:

$$1\,As + 4\,Zn + 4\,O + 11\,H \overset{\checkmark}{=} 1\,As + 4\,Zn + 4\,O + 11\,H$$

   - Charge:

$$8(+1) \overset{\checkmark}{=} 4(+2)$$

The balanced chemical equation (both for charge and for atoms) for this reaction is therefore:

$$H_3AsO_4\,(aq) + 4\,Zn\,(s) + 8\,H^+\,(aq) \longrightarrow AsH_3\,(g) + 4\,Zn^{2+}\,(aq) + 4\,H_2O\,(l)$$

? Exercise 20.2.1: Oxidizing Copper

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$CuS\,(s) + H^+\,(aq) + NO_3^-\,(aq) \longrightarrow Cu^{2+}\,(aq) + NO\,(g) + SO_4^{2-}\,(aq)$$

Answer

$$3\,CuS\,(s) + 8\,H^+\,(aq) + 8\,NO_3^-\,(aq) \rightarrow 3\,Cu^{2+}\,(aq) + 8\,NO\,(g) + 3\,SO_4^{2-}\,(aq) + 4\,H_2O\,(l)$$

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 20.2.2.

✓ Example 20.2.2: Balancing in Basic Solution

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$Al\,(s) + H_2O\,(l) \rightarrow [Al(OH)_4]^-\,(aq) + H_2\,(g)$$

Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given above for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

We will apply the same procedure used in Example 20.2.1, but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.

2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $[\mathrm{Al(OH)_4}]^-$. The oxidation state of hydrogen changes from +1 in $\mathrm{H_2O}$ to 0 in $\mathrm{H_2}$. Aluminum is oxidized, while hydrogen is reduced:

$$\overset{0}{Al}_{(s)} + \overset{+1}{H}_2O_{(aq)} \rightarrow [\overset{+3}{Al}(OH)_4]^-_{(aq)} + \overset{0}{H}_{2\,(g)}$$

3. Write separate equations for oxidation and reduction.
   - Reduction:

$$\overset{+1}{H} + e^- \rightarrow \overset{0}{H}\ (in\ H_2)$$

   - Oxidation:

$$\overset{0}{Al} \rightarrow \overset{+3}{Al} + 3e^-$$

4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:
   - Reduction:

$$3\,\mathrm{H^+} + 3\,\mathrm{e^-} \longrightarrow 3\,\mathrm{H^0}\ (in\ \mathrm{H_2})$$

   - Oxidation:

$$\mathrm{Al^0} \longrightarrow \mathrm{Al^{3+}} + 3\,\mathrm{e^-}$$

5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of $\mathrm{H_2O}$ contains two protons, in this case, $3\,\mathrm{H^+}$ corresponds to $\frac{3}{2}\,\mathrm{H_2O}$. Similarly, each molecule of hydrogen gas contains two H atoms, so $3\,\mathrm{H}$ corresponds to $\frac{3}{2}\,\mathrm{H_2}$.
   - Reduction:

$$\tfrac{3}{2}\,\mathrm{H_2O} + 3\,\mathrm{e^-} \longrightarrow \tfrac{3}{2}\,\mathrm{H_2}$$

   - Oxidation:

$$\mathrm{Al} \longrightarrow [\mathrm{Al(OH)_4}]^- + 3\,\mathrm{e^-}$$

6. Adding the equations and canceling the electrons gives

$$\mathrm{Al} + \tfrac{3}{2}\,\mathrm{H_2O} + \cancel{3\,\mathrm{e^-}} \longrightarrow [\mathrm{Al(OH)_4}]^- + \tfrac{3}{2}\,\mathrm{H_2} + \cancel{3\,\mathrm{e^-}}$$

$$\mathrm{Al} + \tfrac{3}{2}\,\mathrm{H_2O} \longrightarrow [\mathrm{Al(OH)_4}]^- + \tfrac{3}{2}\,\mathrm{H_2}$$

   To remove the fractional coefficients, multiply both sides of the equation by 2:

$$2\,\mathrm{Al} + 3\,\mathrm{H_2O} \rightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

7. The right side of the equation has a total charge of −2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two $\mathrm{OH^-}$ ions to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH^-} + 3\,\mathrm{H_2O} \longrightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three $\mathrm{H_2O}$ molecules to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH^-} + 6\,\mathrm{H_2O} \longrightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

9. Be sure the equation is balanced:
   1. Atoms:

$$2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H} \overset{\checkmark}{=} 2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H}$$

   2. Charge:

$$(2)(0) + (2)(-1) + (6)(0) \overset{\checkmark}{=} (2)(-1) + (3)(0)$$

The balanced chemical equation is therefore

$$2\,\mathrm{Al\,(s)} + 2\,\mathrm{OH^-\,(aq)} + 6\,\mathrm{H_2O\,(l)} \rightarrow 2\,\mathrm{[Al(OH)_4]^-\,(aq)} + 3\,\mathrm{H_2\,(g)}$$

Thus 3 mol of $\mathrm{H_2}$ gas are produced for every 2 mol of Al consumed.

? Exercise 20.2.2: Reducing Manganese in permanganate

The permanganate ion reacts with nitrite ion in basic solution to produce manganese (IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

Answer

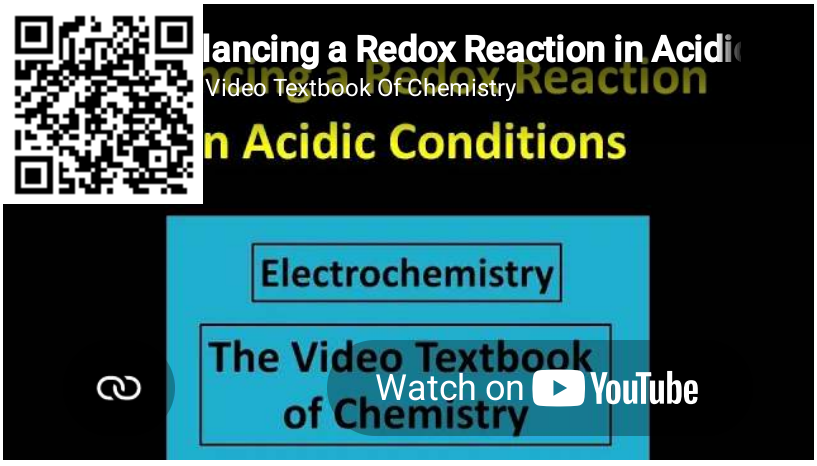
$$2\,\mathrm{MnO_4^-\,(aq)} + 3\,\mathrm{NO_2^-\,(aq)} + \mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{MnO_2\,(s)} + 3\,\mathrm{NO_3^-\,(aq)} + 2\,\mathrm{OH^-\,(aq)}$$

As suggested in Examples 20.2.1 and 20.2.2, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as $\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$, $\mathrm{MnO_4^-}$, $\mathrm{Cr_2O_7^{2-}}$, and $\mathrm{UF_6}$) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as $\mathrm{CH_4}$, $\mathrm{NH_3}$, $\mathrm{H_2S}$, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

> *Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.*



Balancing a Redox Reaction in Acidic Conditions: Balancing a Redox Reaction in Acidic Conditions (opens in new window) [youtu.be]

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance

oxidation–reduction reactions in solution using the oxidation state method, in which the overall reaction is separated into an oxidation equation and a reduction equation.

Contributors and Attributions

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20.3: Voltaic (or Galvanic) Cells- Generating Electricity from Spontaneous Chemical Reactions

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying redox chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$\mathrm{Zn\,(s) + Br_2\,(aq)\ \rightarrow Zn^{2+}\,(aq) + 2\,Br^-\,(aq)}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2\,(aq) + 2\,e^-\ \rightarrow 2\,Br^-\,(aq)}$$

oxidation half-reaction:

$$\mathrm{Zn\,(s)\ \rightarrow Zn^{2+}\,(aq) + 2\,e^-}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 20.3.1). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> *In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).*

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 20.3.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the

cathode). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

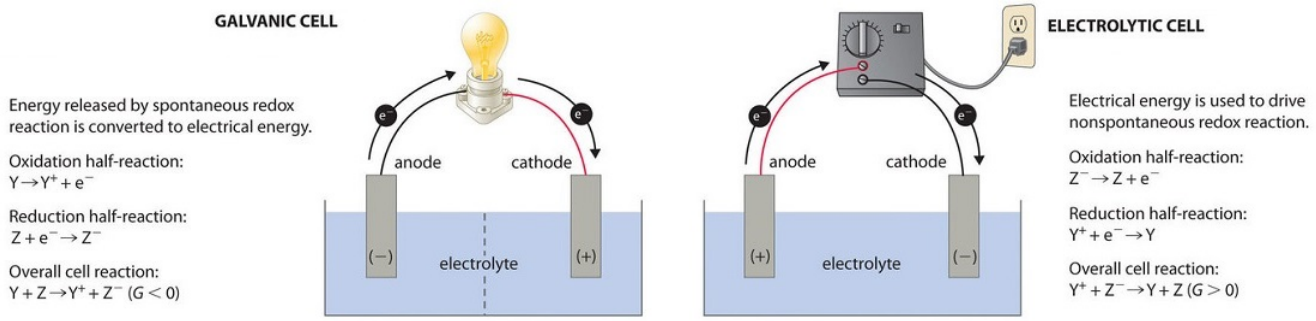


Figure 20.3.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s) \tag{20.3.1}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.



Figure 20.3.2: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $Zn^{2+}\,(aq)$ 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. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure 20.3.3*a*. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of 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 solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure 20.3.3*b*). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

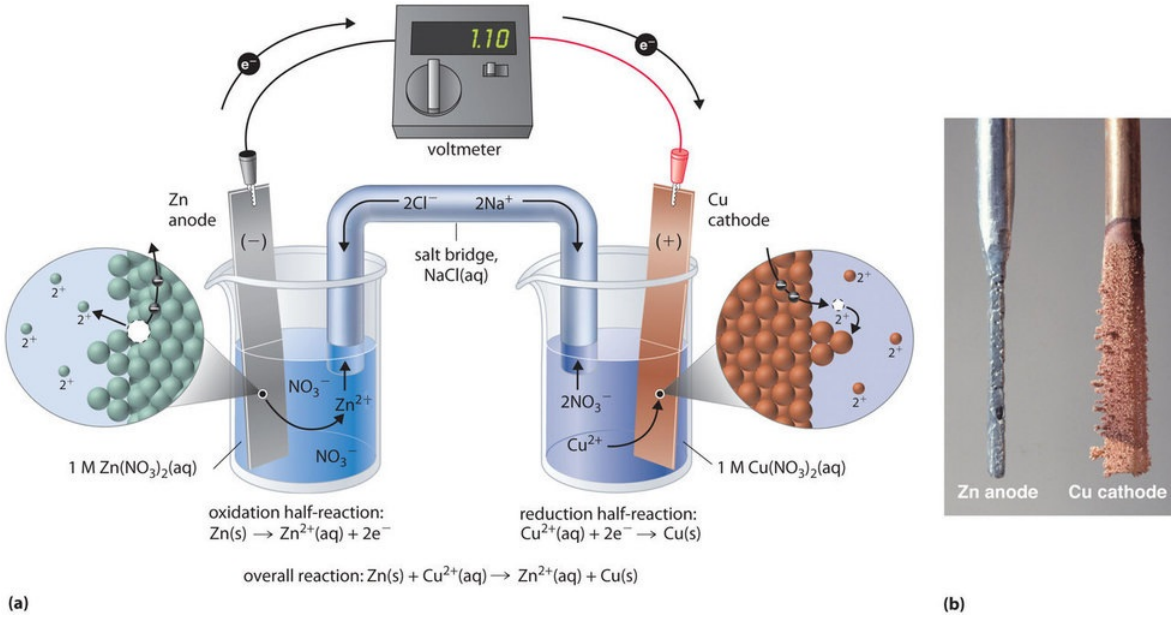


Figure 20.3.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give $Zn^{2+}(aq)$ ions, while the Cu cathode gains mass as $Cu^{2+}(aq)$ ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure 20.3.3*a*). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 20.3.1.

> *A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.*

Example 20.3.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3\,\mathrm{Sn\,(s)} + 2\,\mathrm{NO_3^-\,(aq)} + 8\,\mathrm{H^+\,(aq)} \rightarrow 3\,\mathrm{Sn^{2+}\,(aq)} + 2\,\mathrm{NO\,(g)} + 4\,\mathrm{H_2O\,(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$\mathrm{NO_3^-\,(aq)} + 4\,\mathrm{H^+\,(aq)} + 3\,\mathrm{e^-} \longrightarrow \mathrm{NO\,(g)} + 2\,\mathrm{H_2O\,(l)}$$

oxidation:

$$\mathrm{Sn\,(s)} \longrightarrow \mathrm{Sn^{2+}\,(aq)} + 2\,\mathrm{e^-}$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

Exercise 20.3.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of $\mathrm{MnO_4^-}$ in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of $\mathrm{Sn^{2+}}$ in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2\,\mathrm{MnO_4^-(aq)} + 5\,\mathrm{Sn^{2+}(aq)} + 16\,\mathrm{H^+(aq)} \rightarrow 2\,\mathrm{Mn^{2+}(aq)} + 5\,\mathrm{Sn^{4+}(aq)} + 8\,\mathrm{H_2O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer a

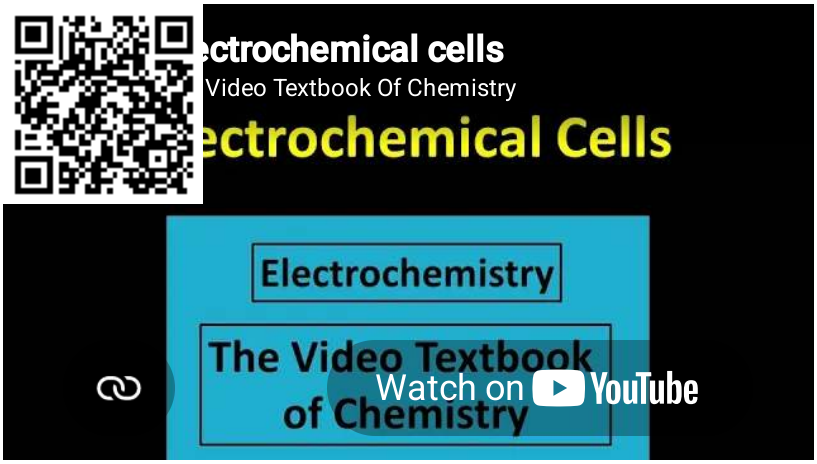
$$\mathrm{MnO_4^-(aq)} + 8\,\mathrm{H^+(aq)} + 5\,\mathrm{e^-} \rightarrow \mathrm{Mn^{2+}(aq)} + 4\,\mathrm{H_2O(l)}$$
$$\mathrm{Sn^{2+}(aq)} \rightarrow \mathrm{Sn^{4+}(aq)} + 2\,\mathrm{e^-}$$

Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer 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.



Electrochemical Cells: Electrochemical Cells(opens in new window) [youtu.be]

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the $\mathrm{Zn/Cu}$ cell shown in Figure $20.3.3a$ is written as follows:

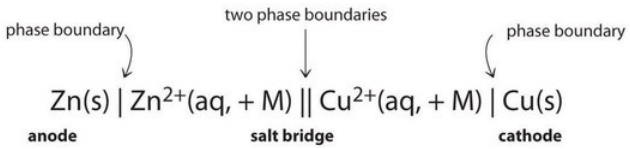


Figure 20.3.4: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$\mathrm{Pt(s)\ |\ H_2(g)\ |\ HCl(aq,\ 1\,M)\ |\ AgCl(s)\ Ag(s)}$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

$$\mathrm{AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)}$$

anode reaction:

$$\mathrm{\tfrac{1}{2}\,H_2(g) \longrightarrow H^+(aq) + e^-}$$

overall:

$$\mathrm{AgCl(s) + \tfrac{1}{2}\,H_2(g) \longrightarrow Ag(s) + Cl^- + H^+(aq)}$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

Example 20.3.2

Draw a cell diagram for the galvanic cell described in Example 20.3.1. The balanced chemical reaction is as follows:

$$\mathrm{3\,Sn(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow 3\,Sn^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)}$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\mathrm{Sn(s)\,|\,Sn^{2+}(aq)}$. We could include $\mathrm{H_2SO_4(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\,|\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

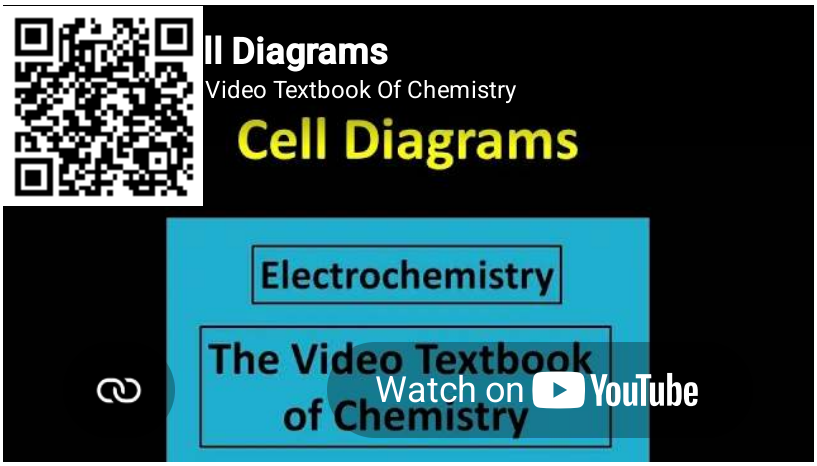
Exercise 20.3.2

Draw the cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:

$$Mg(s) + 2\,Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\,Ag(s)$$

Answer

$$Mg(s)\ |Mg^{2+}(aq,\ 1\,M\ )\,||\,Ag^+(aq,\ 1\ M)\,|\,Ag(s)$$



Cell Diagrams: Cell Diagrams(opens in new window) [youtu.be]

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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20.4: Standard Reduction 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.

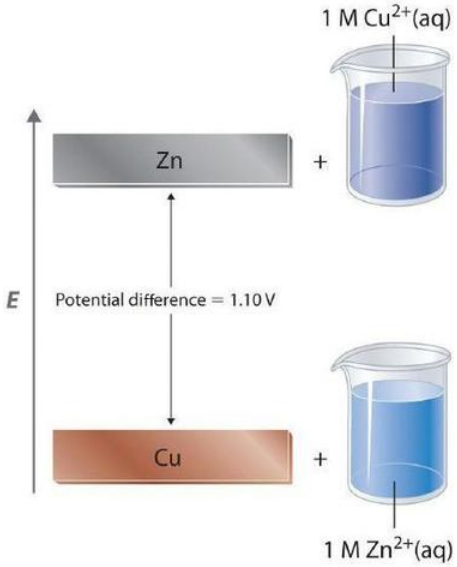


Figure 20.4.1: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 20.4.1 but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

> *Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**; recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E°= 0.59\ V \tag{20.4.1}$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ($E°_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{20.4.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 20.4.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

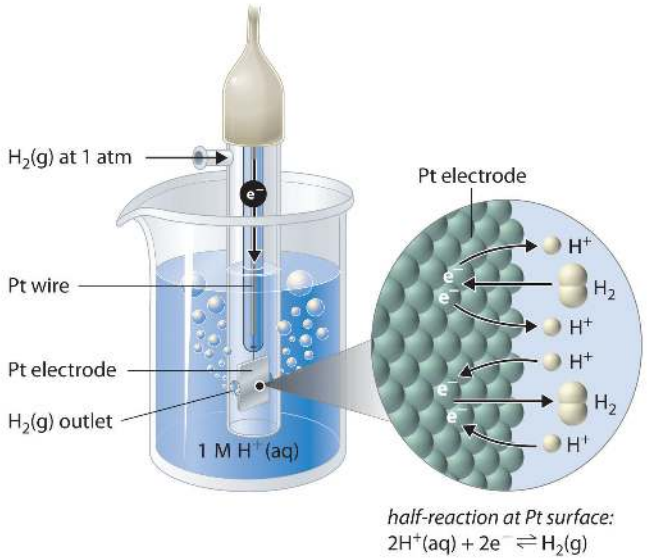


Figure 20.4.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 20.4.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{20.4.3}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

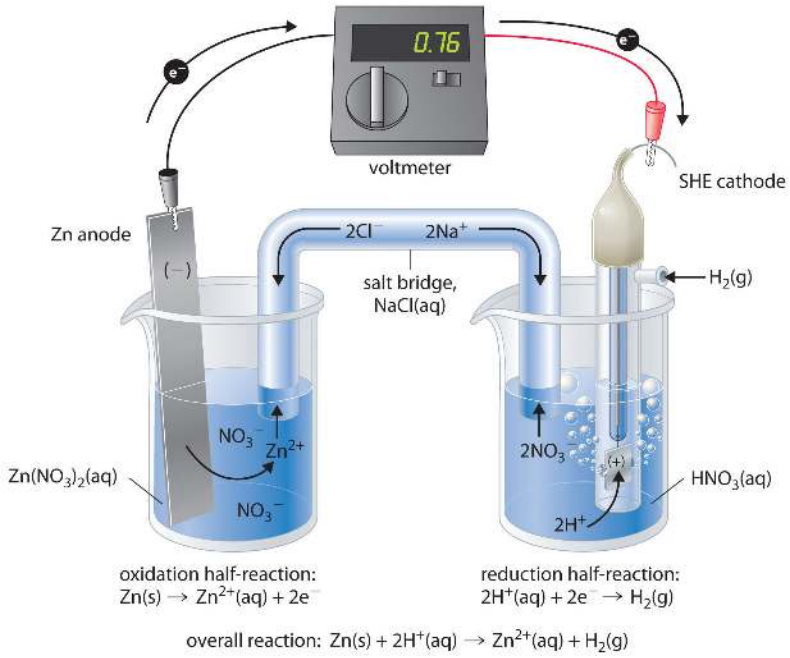


Figure 20.4.3: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form Zn^{2+}(aq) ions while H^+(aq) ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Figure 20.4.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{20.4.4}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E°_{cathode} = 0V \tag{20.4.5}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E°_{anode} = -0.76\ V \tag{20.4.6}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{20.4.7}$$

We then use Equation 20.4.2 to calculate the cell potential

$$\begin{aligned} E°_{cell} &= E°_{cathode} - E°_{anode} \\ &= 0.76\ V \end{aligned}$$

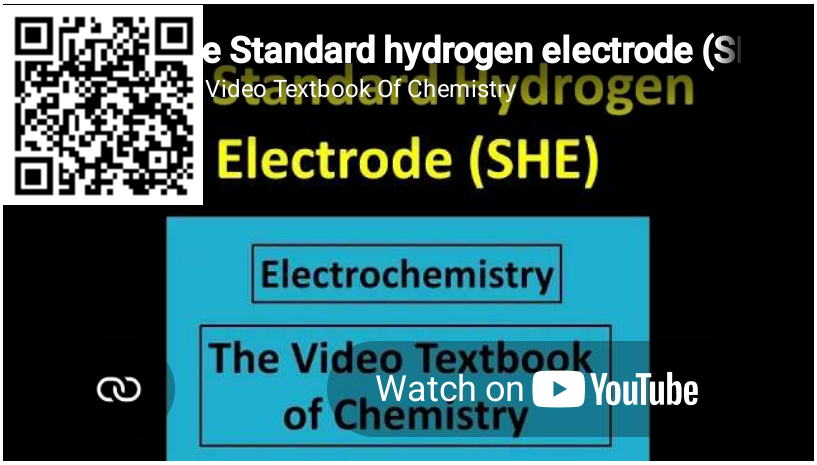
Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for Zn^{2+}(aq) + $2e^-$ → Zn(s) is −0.76 V, which means that the

standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain

$$E°_{cell} : 0\,V - (-0.76\,V) = 0.76\,V$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*



The Standard Hydrogen Electrode (SHE): The Standard Hydrogen Electrode (SHE)(opens in new window) [youtu.be]

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure 20.4.3 but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{20.4.8}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E°_{cathode} = 0.34\ V \tag{20.4.9}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E°_{anode} = 0\ V \tag{20.4.10}$$

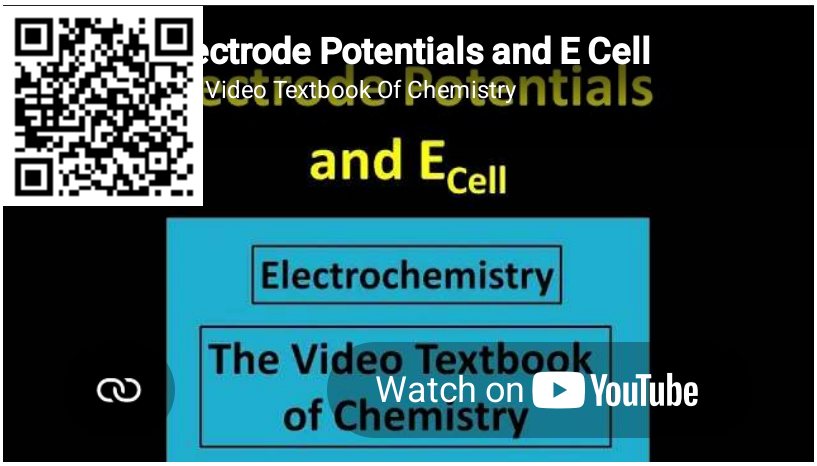
- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{20.4.11}$$

We then use Equation 20.4.2 to calculate the cell potential

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$= 0.34\ V$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.



Electrode Potentials and ECell: Electrode and Potentials and Ecell(opens in new window) [youtu.be]

Balancing Redox Reactions Using the Half-Reaction Method

In Section 4.4, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al_{(s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + H_{2(g)} \tag{20.4.12}$$

In this reaction, $Al_{(s)}$ is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed Table P1, we find the corresponding half-reactions that describe the reduction of H^+ ions in water to $H_2$and the oxidation of Al to Al^{3+} in basic solution:

- reduction:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{20.4.13}$$

- oxidation:

$$Al_{(s)} + 4OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3e^- \tag{20.4.14}$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 20.4.13, two H^+ ions gain one electron each in the reduction; in Equation 20.4.14, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 20.4.13) by 3 and the oxidation half-reaction (Equation 20.4.14) by 2 to give the same number of electrons in both half-reactions:

- reduction:

$$6H_2O_{(l)} + 6e^- \rightarrow 6OH^-_{(aq)} + 3H_{2(g)} \tag{20.4.15}$$

- oxidation:

$$2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 6e^- \tag{20.4.16}$$

Adding the two half-reactions,

$$6H_2O_{(l)} + 2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-4(aq) + 3H_{2(g)} + 6OH^-_{(aq)} \tag{20.4.17}$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O_{(l)} + 2Al_{(s)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.4.18}$$

We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H \tag{20.4.19}$$

The atoms also balance, so Equation 20.4.18 is a balanced chemical equation for the redox reaction depicted in Equation 20.4.12.

> *The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.*

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1, but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 20.4.12, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} \tag{20.4.20}$$

- oxidation:

$$Al_{(s)} \rightarrow Al(OH)^-_{4(aq)} \tag{20.4.21}$$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{20.4.22}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} \tag{20.4.23}$$

Balancing H atoms by adding H^+, we obtain the following:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{20.4.24}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} \tag{20.4.25}$$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + H_2O_{(l)} \tag{20.4.26}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} + 3e^- \tag{20.4.27}$$

Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 20.4.26 (the reductive half-reaction) by 3 and Equation 20.4.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

- reduction:

$$3OH^-_{(aq)} + 9H^+_{(aq)} + 6e^- \rightarrow 3H_{2(g)} + 3H_2O_{(l)} \tag{20.4.28}$$

- oxidation:

$$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} + 8H^+_{(aq)} + 6e^- \tag{20.4.29}$$

Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$2Al_{(s)} + 5H_2O_{(l)} + 3OH^-_{(aq)} + H^+_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.4.30}$$

We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$2Al_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{20.4.31}$$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 20.4.31 is identical to Equation 20.4.18, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

Example 20.4.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7{}^{2-}$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}\,(aq)$ complex and brown $I_2\,(aq)$ ions (Figure 20.4.4):

$$Cr_2O_7{}^{2-}\,(aq) + I^-\,(aq) \longrightarrow Cr^{3+}\,(aq) + I_2\,(aq)$$

Balance this equation using half-reactions.

Given: redox reaction and Table P1

Asked for: balanced chemical equation using half-reactions

Strategy:

Follow the steps to balance the redox reaction using the half-reaction method.

Solution

From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:

- reduction:

$$\mathrm{Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)}$$

- oxidation:

$$\mathrm{2\,I^-(aq) \longrightarrow I_2(aq) + 2\,e^-}$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:

$$\mathrm{6\,I^-(aq) \longrightarrow 3\,I_2(aq) + 6\,e^-}$$

Adding the two half-reactions and canceling electrons,

$$\mathrm{Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,I^-(aq) \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) + 3\,I_2(aq)}$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$(-2) + 14 + (-6) = +6$$

$$+6 \overset{\checkmark}{=} +6$$

and atoms

$$\mathrm{2\,Cr + 7\,O + 14\,H + 6\,I \overset{\checkmark}{=} 2\,Cr + 7\,O + 14\,H + 6\,I}$$

Both the charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Table P1.

Step 1: Chromium is reduced from $\mathrm{Cr^{6+}}$ in $\mathrm{Cr_2O_7^{2-}}$ to $\mathrm{Cr^{3+}}$, and $\mathrm{I^-}$ ions are oxidized to $\mathrm{I_2}$. Dividing the reaction into two half-reactions,

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow Cr^{3+}_{(aq)}$$

- oxidation:

$$I^-_{(aq)} \rightarrow I_{2(aq)}$$

Step 2: Balancing the atoms other than oxygen and hydrogen,

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow 2Cr^{3+}_{(aq)}$$

- oxidation:

$$2I^-_{(aq)} \rightarrow I_{2(aq)}$$

We now balance the O atoms by adding $\mathrm{H_2O}$—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

Next we balance the H atoms by adding $\mathrm{H^+}$ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

- reduction:

$$Cr_2O_{7(aq)}^{2-} + 14H_{(aq)}^{+} \rightarrow 2Cr_{(aq)}^{3+} + 7H_2O_{(l)}$$

Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

- reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- oxidation: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

- oxidation: $6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

$$\mathrm{Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,I^-\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l) + 3\,I_2\,(aq)}$$

Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

? Exercise 20.4.1

Copper is found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid ($\mathrm{HNO_3}$), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$$\mathrm{CuS\,(s) + HNO_3\,(aq) \rightarrow NO\,(g) + CuSO_4\,(aq)}$$

Balance this equation using the half-reaction method.



Covellite (also known as covelline) is a rare copper sulfide mineral with an indigo blue color that is ubiquitous in copper ores. (CC SA-BY 3.0;'Didier Descouens).

Answer

$$\mathrm{3\,CuS\,(s) + 8\,HNO_3\,(aq) \longrightarrow 8\,NO\,(g) + 3\,CuSO_4\,(aq) + 4\,H_2O\,(l)}$$

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{20.4.32}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

- cathode:

$$Cu_{(aq)}^{2+} + 2e^- \rightarrow Cu_{(s)} \qquad E°_{cathode} = 0.34\ V \tag{20.4.33}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E°_{anode} = -0.76\ V \tag{20.4.34}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{20.4.35}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 1.10\ V$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 20.4.2 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> *A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.*

Example 20.4.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$\text{cathode: } Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

$$\text{anode: } Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$$

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 20.4.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 20.4.2:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$0.27\,V = E°°_{cathhode} - (-0.55\,V)$$
$$E°_{cathode} = -0.28\,V$$

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 20.4.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $\mathrm{Hg(CH_3CO_2)_2}$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $\mathrm{MgCl_2}$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $\mathrm{Hg^{2+}\,(aq) + 2\,e^- \longrightarrow Hg\,(l)}$
- anode: $\mathrm{Mg\,(s) \longrightarrow Mg^{2+}\,(aq) + 2\,e^-}$

If the potential for the oxidation of Mg to $\mathrm{Mg^{2+}}$ is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the cathode?

Answer

0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

> *The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.*

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)} \tag{20.4.36}$$

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 20.4.5. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt_{(s)} \mid Hg_2Cl_{2(s)} \mid KCl_{(aq,sat)} \tag{20.4.37}$$

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-(aq) \tag{20.4.38}$$

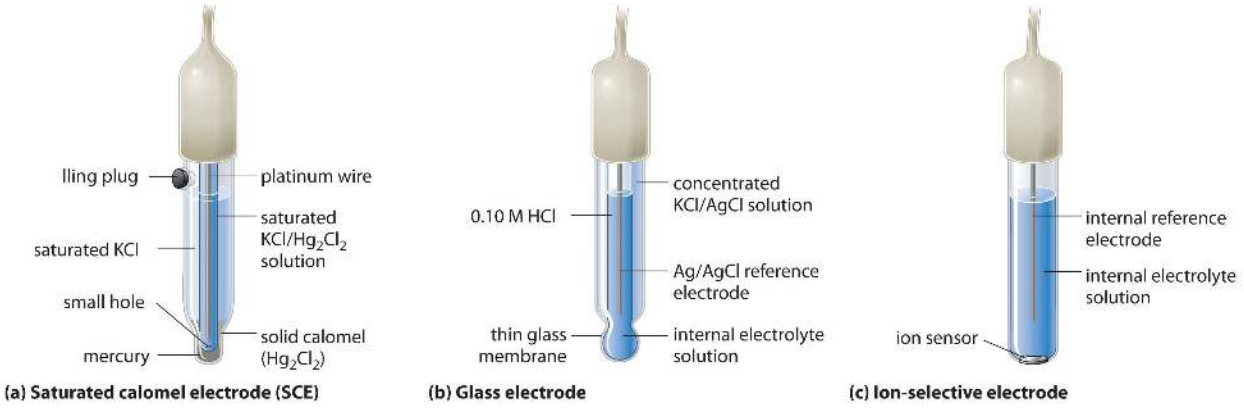


Figure 20.4.5: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution. (CC BY-SA-NC; anonymous)

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 20.4.5. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that $pH = -\log[H^+]$):

$$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH \tag{20.4.39}$$

The voltage E′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 20.4.5). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 20.4.1.

Table 20.4.1: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction. \(E°_{cell} = E°_{cathode} − E°_{anode} \nonumber \] The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} − E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

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20.5: Cell Potential, Gibbs Energy, and the Equilibrium Constant

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 x 10^{18} electrons. Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s). Voltage is the potential difference required to move a charge through a circuit. By definition a coulomb of charge flowing through a potential difference of 1 V will require a 1J of energy

$$\frac{1\ J}{1\ V} = 1\ C$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{aligned} F &= (1.60218 \times 10^{-19}\ \mathrm{C}) \left(\frac{6.02214 \times 10^{23}\ J}{1\ \mathrm{mol\ e^-}} \right) \\ &= 9.64833212 \times 10^{4}\ \mathrm{C/mol\ e^-} \\ &\simeq 96,485\ C/(\mathrm{mol\ e^-}) \end{aligned}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{20.5.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 20.5.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG^o for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^o, write the overall reaction and calculate E°_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Then use Equation 20.5.1 to calculate ΔG^o. If ΔG^o is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E^o. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E^o values:

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$	$E^\circ_{anode} = 1.09\ V$

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:

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-$	$E^\circ_{anode} = 1.09\ V$
overall:	$Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)$	$E^\circ_{cell} = 0.27\ V$

B

We can now calculate ΔG° using Equation 20.5.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned}\Delta G^\circ &= -(n)(F)(E^\circ_{cell}) \\ &= -(6\ \text{mole})[96,485\ \text{J}/(\text{V}\cdot\text{mol})(0.27\ \text{V})] \\ &= -15.6 \times 10^4\ \text{J} \\ &= -156\ \text{kJ/mol}\ Cr_2O_7^{2-}\end{aligned}$$

Thus ΔG^o is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

Exercise 20.5.1

Use the data in Table P2 to calculate ΔG^o for the reduction of ferric ion by iodide:

$$2\,Fe^{3+}\,(aq) + 2\,I^-\,(aq) \longrightarrow 2\,Fe^{2+}\,(aq) + I_2\,(s)$$

Is the reaction spontaneous?

Answer

−44 kJ/mol I_2; yes

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 $Fe^{3+}\,(aq)$ to $Fe\,(s)$ is not listed in the table, but two related reductions are given:

$$Fe^{3+}\,(aq) + e^- \longrightarrow Fe^{2+}\,(aq) \quad E^\circ = +0.77V$$

$$Fe^{2+}\,(aq) + 2\,e^- \longrightarrow Fe\,(s) \quad E^\circ = -0.45V$$

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:

$$\begin{aligned}
Fe^{3+}\,(aq) + e^- &\rightarrow Fe^{2+}\,(aq) && \Delta G^\circ = -(1)(F)(0.77\text{ V}) \\
Fe^{2+}\,(aq) + 2\,e^- &\rightarrow Fe\,(s) && \Delta G^\circ = -(2)(F)(-0.45\text{ V}) \\
Fe^{3+}\,(aq) + 3\,e^- &\rightarrow Fe\,(s) && \Delta G^\circ = [-(1)(F)(0.77\text{ V})] + [-(2)(F)(-0.45\text{ V})]
\end{aligned}$$

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F\,[(-0.77V) + (-2)(-0.45V)] = F(0.13V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 20.5.1 and solving for E^o gives the following:

$$\begin{aligned}
\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\
F(0.13\text{ V}) &= -(3)(F)(E^\circ_{\text{cell}}) \\
E^\circ &= -\frac{0.13\text{ V}}{3} = -0.043\text{ V}
\end{aligned}$$

This value of E^o is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> *Values of E^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^\circ = -RT \ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 20.5.1), we can write

$$-nFE^{\circ}_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^{\circ}_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{20.5.2}$$

For $T = 298\ K$, Equation 20.5.2 can be simplified as follows:

$$\begin{aligned} E^{\circ}_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \\ &= \left[\frac{[8.314\ \text{J/(mol} \cdot \text{K)(298 K)}]}{n[96,485\ \text{J/(V} \cdot \text{mol)}]}\right] 2.303 \log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right) \log K \end{aligned} \tag{20.5.3}$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Example 20.5.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E^{o}_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Use Equation 20.5.3 to solve for $\log K$ and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

cathode:	$\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$	$E^{\circ}_{\text{cathode}} = 1.69\ \text{V}$
anode:	$\text{Pb}(s) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) + 2\text{e}^-$	$E^{\circ}_{\text{anode}} = -0.36\ \text{V}$
overall:	$\text{Pb}(s) + \text{PbO}_2(s) + 2\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$	$E^{\circ}_{\text{cell}} = 2.05\ \text{V}$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 20.5.3 for log K and inserting the values of n and E^{o},

$$\log K = \frac{nE^{\circ}}{0.0591\ \text{V}} = \frac{2(2.05\ \text{V})}{0.0591\ \text{V}} = 69.37$$

$$K = 2.3 \times 10^{69}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

Exercise 20.5.2

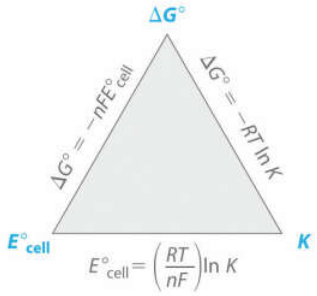
Use the data in Table P2 to calculate the equilibrium constant for the reaction of $\text{Sn}^{2+}(aq)$ with oxygen to produce $\text{Sn}^{4+}(aq)$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2\,\text{Sn}^{2+}(aq) + \text{O}_2(g) + 4\,\text{H}^+(aq) \rightleftharpoons 2\,\text{Sn}^{4+}(aq) + 2\,\text{H}_2\text{O}(l)$$

Answer

5.7×10^{72}

Figure 20.5.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity (ΔG° < 0). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.



ΔG°	E°cell	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 20.5.1: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and $E°_{cell}$. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and $E°_{cell}$ and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E^o is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E^o is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium .

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of E°.

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20.6: Cell Potential and Concentration

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:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{20.6.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^o = -nFE^o_{cell}$ (under standard conditions). Substituting these expressions into Equation 20.6.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT \ln Q \tag{20.6.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{20.6.3}$$

Equation 20.6.3 is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation 20.6.3 reduces to Equation 20.6.4 and 20.6.5 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{20.6.4}$$

since

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{20.6.5}$$

Substituting the values of the constants into Equation 20.6.3 with $T = 298\ K$ and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential ($E°_{cell}$), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{20.6.6}$$

The Power of the Nernst Equation

The Nernst Equation (20.6.3) can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 20.6.6 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 20.6.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 20.6.1

The following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which means that $\Delta G° < 0$):

$$2\,Ce^{4+}\,(aq) + 2\,Cl^{-}\,(aq) \longrightarrow 2\,Ce^{3+}\,(aq) + Cl_2\,(g) \qquad E^{\circ}_{cell} = 0.25\,V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}]$ = 0.013 M, $[Ce^{3+}]$ = 0.60 M, $[Cl^{-}]$ = 0.0030 M, P_{Cl_2} = 1.0 atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 20.6.6 instead of Equation 20.6.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^{-} \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 20.6.6,

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[\text{Ce}^{3+}]^2 P_{\text{Cl}_2}}{[\text{Ce}^{4+}]^2[\text{Cl}^{-}]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and ΔG = 0). The composition specified is that of an equilibrium mixture

Exercise 20.6.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,MnO_2\,(s) + 3\,O_2\,(g) + 4\,OH^{-}\,(aq) \longrightarrow 4\,MnO_4^{-}\,(aq) + 2\,H_2O\,(l) \quad E°_{cell} = -0.20\,V$$

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

E_{cell} = −0.22 V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E°cell = 1.10V \tag{20.6.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0 × 10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 20.6.6:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \tag{20.6.8}$$

$$= 1.10\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log \left(\frac{1.0 \times 10^{-6}}{1.0}\right) = 1.28\ \text{V} \tag{20.6.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio Q = $[Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so Q = 1 and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0×10^{-6} M Cu^{2+}), Q = 1.0×10^6, and the cell potential will be reduced to 0.92 V.

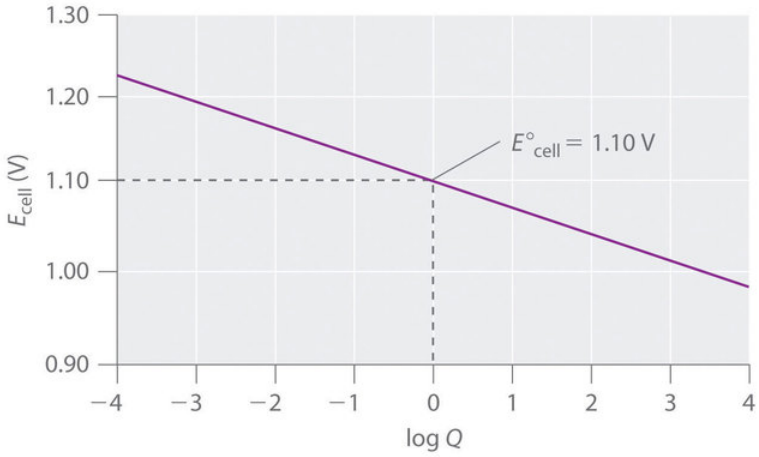


Figure 20.6.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with $\log Q$ over this range is linear with a slope of −0.0591/n, as illustrated in Figure 20.6.1. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when $E_{cell} = 0$ is calculated as follows:

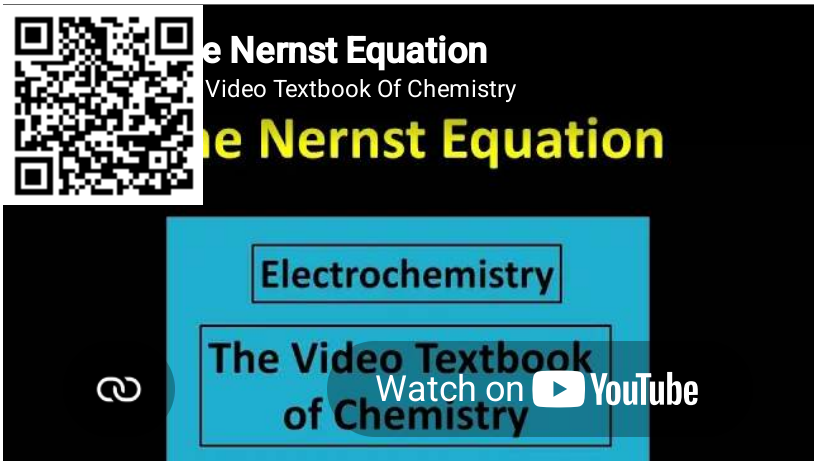
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q = 0 \tag{20.6.10}$$

$$E^\circ = \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{20.6.11}$$

$$\log Q = \frac{E^\circ n}{0.0591\ \text{V}} = \frac{(1.10\ \text{V})(2)}{0.0591\ \text{V}} = 37.23 \tag{20.6.12}$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \tag{20.6.13}$$

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C.



The Nernst Equation: The Nernst Equation (opens in new window) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$\mathrm{Ag(s)\,|\,Ag^+}(aq, 0.010\ M)\,||\,\mathrm{Ag^+}(aq, 1.0\ M)\,|\,\mathrm{Ag\,(s)} \tag{20.6.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag\,(s)} \tag{20.6.15}$$

anode:

$$\mathrm{Ag\,(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{20.6.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{20.6.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

Example 20.6.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.

B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$Mn^{2+}(aq, 2.0\,M) \rightarrow Mn^{2+}(aq, 5.2 \times 10^{-2}\,M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 20.6.6:

$$\begin{aligned} E_{cell} &= E^\circ_{cell} - \left(\frac{0.0591\text{ V}}{n}\right)\log Q \\ &= 0\text{ V} - \left(\frac{0.0591\text{ V}}{2}\right)\log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\text{ V} \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 20.6.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \rightarrow 2\,H_2O\,(l)$$

What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

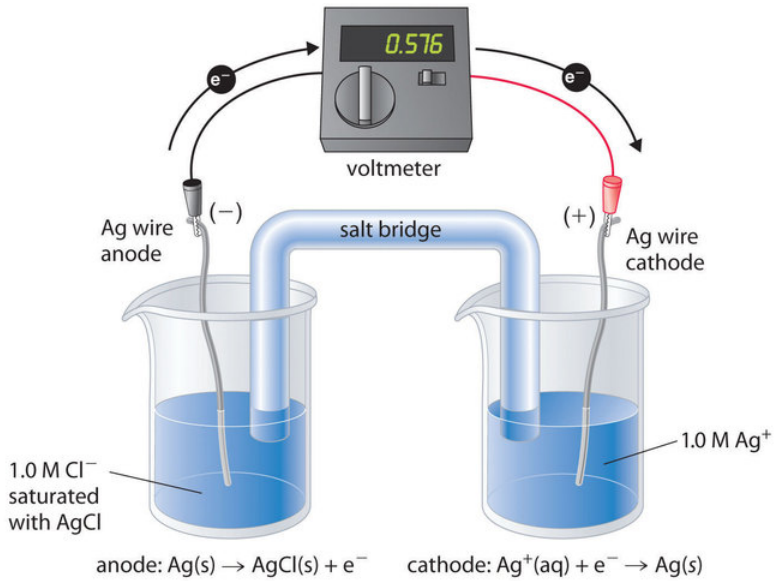


Figure 20.6.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}. (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 20.6.1, which is designed to measure the solubility product of silver chloride:

$$K_{sp} = [Ag^+][Cl^-].$$

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:

$$\begin{aligned}[Ag^+] &= \frac{K_{sp}}{[Cl^-]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}.\end{aligned}$$

The overall cell reaction is as follows:

$$Ag^+(aq, \text{concentrated}) \rightarrow Ag^+(aq, \text{dilute})$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$\begin{aligned}E_{\text{cell}} &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{1}\right) \log\left(\frac{[Ag^+]_{\text{dilute}}}{[Ag^+]_{\text{concentrated}}}\right) \\ &= -0.0591\ \text{V}\ \log\left(\frac{K_{\text{sp}}}{1.0}\right) \\ &= -0.0591\ \text{V}\ \log K_{\text{sp}} \qquad (20.6.18)\end{aligned}$$

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 20.6.18 for K_{sp},

$$\log K_{\text{sp}} = \frac{-E_{\text{cell}}}{0.0591\ \text{V}} = \frac{-0.580\ \text{V}}{0.0591\ \text{V}} = -9.81$$

$$K_{\text{sp}} = 1.5 \times 10^{-10}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

Example 20.6.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 20.6.1, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.

B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$

$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{K_{sp}}{1.0\ M} = K_{sp}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq, concentrated) \rightarrow Pb^{2+}(aq, dilute)$$

so

$$E_{cell} = E^{\circ}_{cell} - \left(\frac{0.0591}{n}\right) \log Q$$

$$0.230\ V = 0\ V - \left(\frac{0.0591\ V}{2}\right) \log \left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ V \log \left(\frac{K_{sp}}{1.0}\right)$$

$$-7.77 = \log K_{sp}$$

$$1.7 \times 10^{-8} = K_{sp}$$

Exercise 20.6.3

A concentration cell similar to the one described in Example 20.6.3 contains a 1.0 M solution of lanthanum nitrate [$La(NO_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer

5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 20.6.3, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated below.

Example 20.6.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$$Zn\,(s)|Zn^{2+}(aq, 1.0\,M)||H^+(aq, ?\,M)|H_2(g, 1.0\,atm)|Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.

B. Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E°=0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 20.6.6), we can calculate $[H^+]$ under nonstandard conditions:

$$\begin{aligned} E_{cell} &= E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right)\log\left(\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}\right) \\ 0.26\ V &= 0.76\ V - \left(\frac{0.0591\ V}{2}\right)\log\left(\frac{(1.0)(1.0)}{[H^+]^2}\right) \\ 16.9 &= \log\left(\frac{1}{[H^+]^2}\right) = \log[H^+]^{-2} = (-2)\log[H^+] \\ 8.46 &= -\log[H^+] \\ 8.5 &= pH \end{aligned}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 20.6.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:

$$Pb_{(s)} \mid Pb^{2+}(aq, ?M) \parallel H^+(aq), 1.0M \mid O_2(g, 1.0atm) \mid Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer

$1.2 \times 10^{-9}\ M$

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.

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20.7: Batteries- Using Chemistry to Generate Electricity

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 20.7.1). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

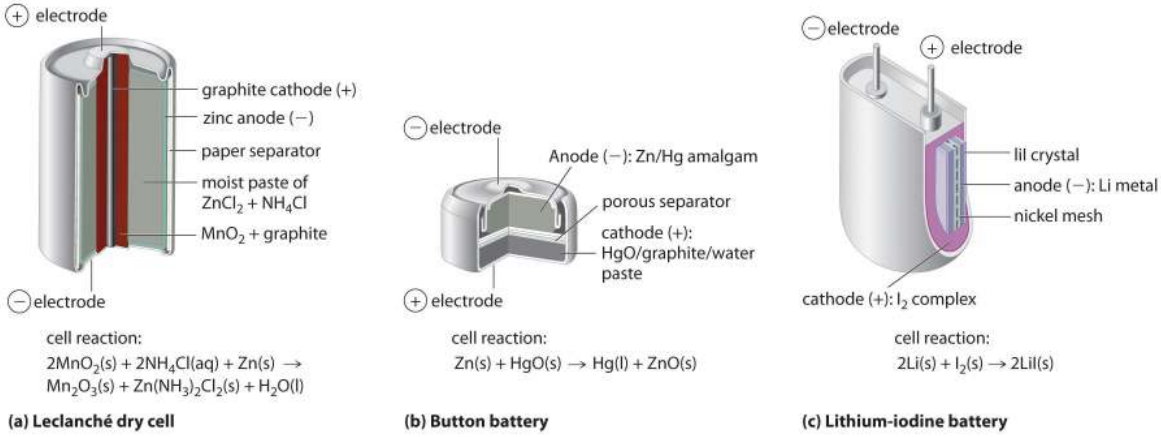


Figure 20.7.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

> The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure 20.7.1). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,MnO_2\,(s) + 2\,NH_4^+\,(aq) + 2\,e^- \longrightarrow Mn_2O_3\,(s) + 2\,NH_3\,(aq) + H_2O\,(l)$$

- anode (oxidation):

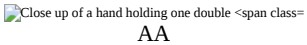
$$\mathrm{Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^-}$$

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:

$$\mathrm{2\,MnO_2\,(s) + 2\,NH_4Cl\,(aq) + Zn\,(s) \longrightarrow Mn_2O_3\,(s) + Zn(NH_3)_2Cl_2\,(s) + H_2O\,(l)} \tag{20.7.1}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the $\mathrm{MnO_2}$ that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with $\mathrm{NH_4Cl}$ in the electrolyte, causing the case to corrode and allowing the contents to leak out.



AA

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Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$\mathrm{2\,MnO_2\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow Mn_2O_3\,(s) + 2\,OH^-\,(aq)}$$

- anode (oxidation):

$$\mathrm{Zn\,(s) + 2\,OH^-\,(aq) \longrightarrow ZnO\,(s) + H_2O\,(l) + 2\,e^-}$$

- overall reaction:

$$\mathrm{Zn\,(s) + 2\,MnO_2\,(s) \longrightarrow ZnO\,(s) + Mn_2O_3\,(s)}$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or $\mathrm{Ag_2O}$ as the oxidant rather than $\mathrm{MnO_2}$ in Figure 20.7.1*b*).



Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$\mathrm{HgO\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow Hg\,(l) + 2\,OH^-\,(aq)}$$

- Anode (mercury battery):

$$\mathrm{Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-}$$

- overall reaction (mercury battery):

$$\mathrm{Zn\,(s) + 2\,HgO\,(s) \longrightarrow 2\,Hg\,(l) + ZnO\,(s)}$$

with $E_{cell} = 1.35\,V$.

- cathode reaction (silver battery):

$$\mathrm{Ag_2O\,(s) + H_2O\,(l) + 2\,e^- \longrightarrow 2\,Ag\,(s) + 2\,OH^-\,(aq)}$$

- anode (silver battery):

$$\mathrm{Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-}$$

- Overall reaction (silver battery):

$$\mathrm{Zn\,(s) + 2\,Ag_2O\,(s) \longrightarrow 2\,Ag\,(s) + ZnO\,(s)}$$

with $E_{cell} = 1.6\,V$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-{}_{(LiI)} \tag{20.7.2}$$

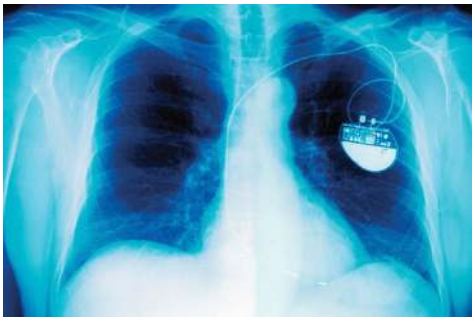
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{20.7.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{20.7.4}$$

with $E_{cell} = 3.5\,V$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure 20.7.1, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure 20.7.2, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

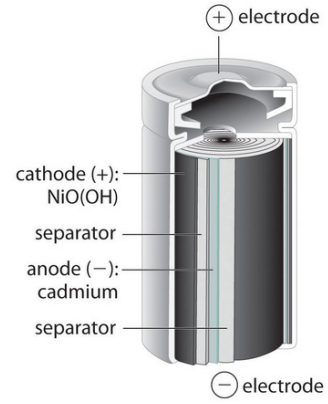


Figure 20.7.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a $NiCad$ battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{20.7.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{20.7.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{20.7.7}$$

$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.

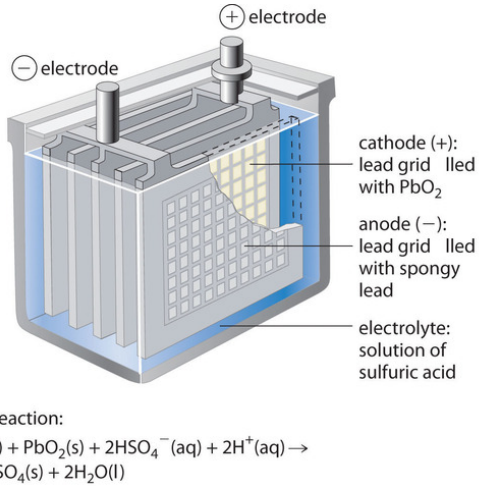


Figure 20.7.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure 20.7.3, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

\[PbO_{2(s)} + HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17} \]

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{20.7.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{20.7.9}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.



A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{20.7.10}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

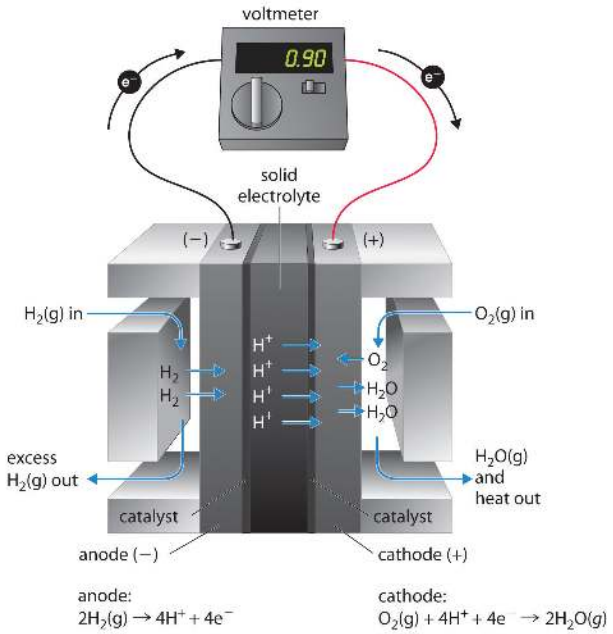


Figure 20.7.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of H_2(g) and O_2(g), as illustrated in Figure 20.7.4. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{20.7.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{20.7.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{20.7.13}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

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20.8: Electrolysis- Driving Non-spontaneous Chemical Reactions with Electricity

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 $20.8.1a$).

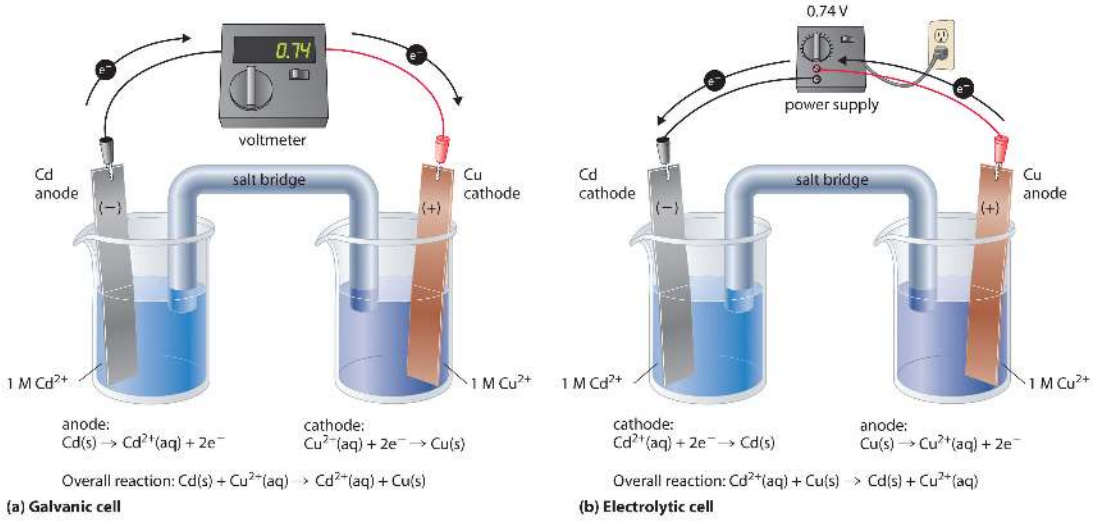


Figure 20.8.1: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) 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 $E°_{cell} = 0.74\ V$

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 20.8.1*b*). 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:

$$\mathrm{Cd^{2+}\,(aq) + 2\,e^-} \rightarrow \mathrm{Cd\,(s)} \tag{20.8.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu\,(s)} \rightarrow \mathrm{Cu^{2+}\,(aq) + 2\,e^-} \tag{20.8.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2+}\,(aq) + Cu\,(s)} \rightarrow \mathrm{Cd\,(s) + Cu^{2+}\,(aq)} \tag{20.8.3}$$

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 20.8.1.

Table 20.8.1: 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:

$$\mathrm{2\,NaCl\,(l)} \rightarrow \mathrm{2\,Na\,(l) + Cl_2\,(g)} \tag{20.8.4}$$

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 20.8.2). 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.

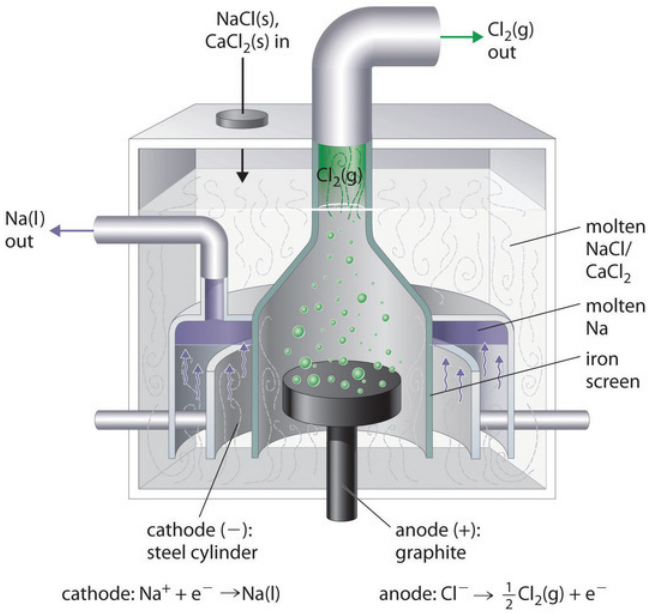


Figure 20.8.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the 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:

$$2\,Al_2O_3\,(l) + 3\,C\,(s) \longrightarrow 4\,Al\,(l) + 3\,CO_2\,(g) \tag{20.8.5}$$

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 20.8.1

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 20.8.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

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 20.8.3).

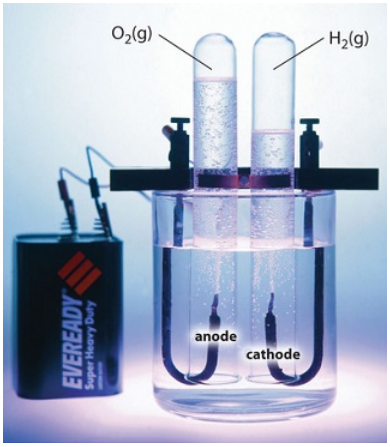


Figure 20.8.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{20.8.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{20.8.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{20.8.8}$$

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:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{\text{O}_2}P^2_{\text{H}_2}) \tag{20.8.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{20.8.10}$$

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 20.8.4.

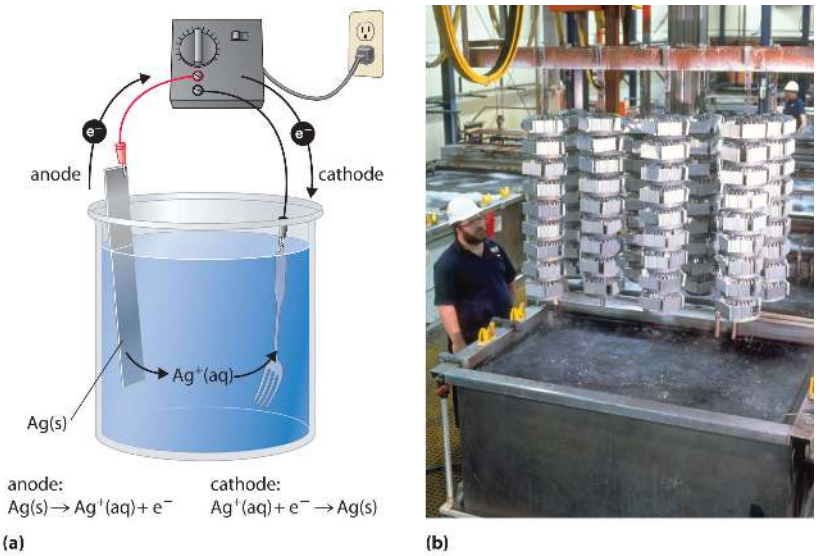


Figure 20.8.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually 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):

$$q = I \times t \tag{20.8.11}$$

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 $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\text{ A})(6.0\text{ min})(60\text{ s/min}) \\ &= 220\text{ A}\cdot\text{s} \\ &= 220\text{ C} \end{aligned}$$

The number of moles of electrons transferred to Cu^{2+} is therefore

$$\begin{aligned} \text{moles e}^- &= \frac{220\text{ C}}{96{,}485\text{ C/mol}} \\ &= 2.3 \times 10^{-3}\text{ mol e}^- \end{aligned}$$

Because two electrons are required to reduce a single 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 20.8.2

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

$$\begin{aligned} \text{amperes} &= \frac{1.78 \times 10^3\text{ C}}{(12.0\text{ h})(60\text{ min/h})(60\text{ s/min})} \\ &= 4.12 \times 10^{-2}\text{ C/s} = 4.12 \times 10^{-2}\text{ A} \end{aligned}$$

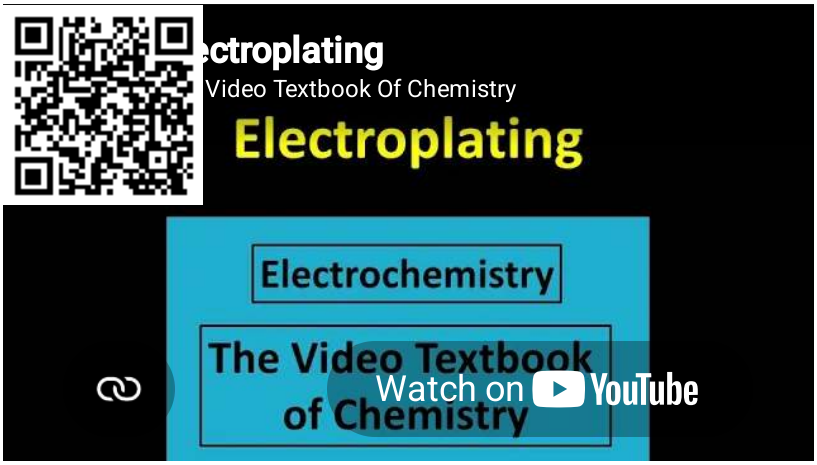
Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise 20.8.2

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

5.8 h



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.

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20.9: Corrosion- Undesirable Redox Reactions

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 ($Fe_2O_3 \cdot x\,H_2O$), commonly known as rust, that does not provide a tight protective film (Figure 20.9.1). 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.

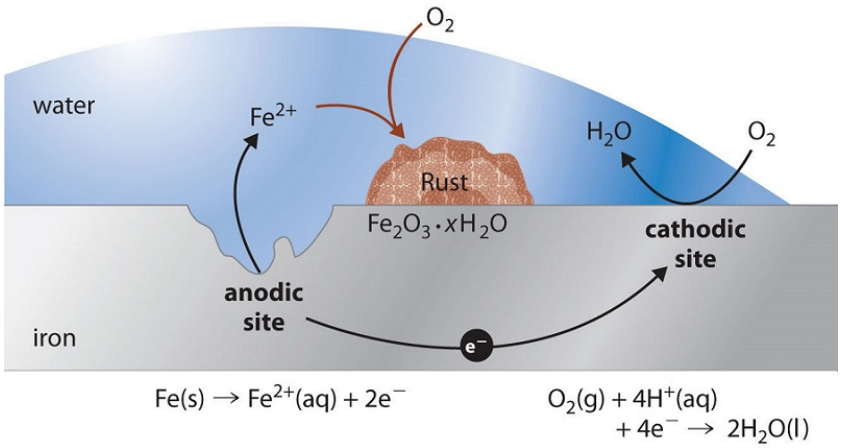


Figure 20.9.1: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons 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•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:

$$O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \longrightarrow 2\,H_2O\,(l)$$

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:

$$\mathrm{2\,Fe\,(s) + O_2\,(g) + 4\,H^+\,(aq) \longrightarrow 2\,Fe^{2+}\,(aq) + 2\,H_2O\,(l)} \tag{20.9.1}$$

with $E^o_{cell} = 1.68\ V$.

The $\mathrm{Fe^{2+}}$ ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing $\mathrm{Fe^{3+}}$, as represented in the following equation:

$$\mathrm{4\,Fe^{2+}\,(aq) + O_2\,(g) + (2 + 4\,x)H_2O \ \rightarrow 2\,Fe_2O_3 \ \cdot x\,H_2O + 4\,H^+\,(aq)} \tag{20.9.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 20.9.1) 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 20.9.2).

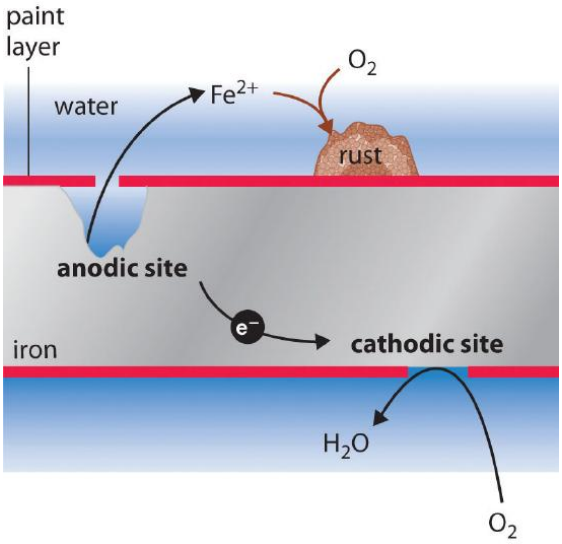


Figure 20.9.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). 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).

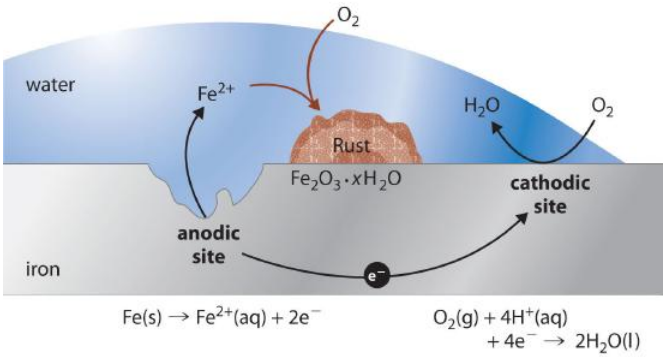


Figure 20.9.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can 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 Sn^{2+} ($E° = −0.14$ V) and 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 20.9.3). 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 $\mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Zn}$) 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:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{20.9.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{20.9.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{20.9.5}$$

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 20.9.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

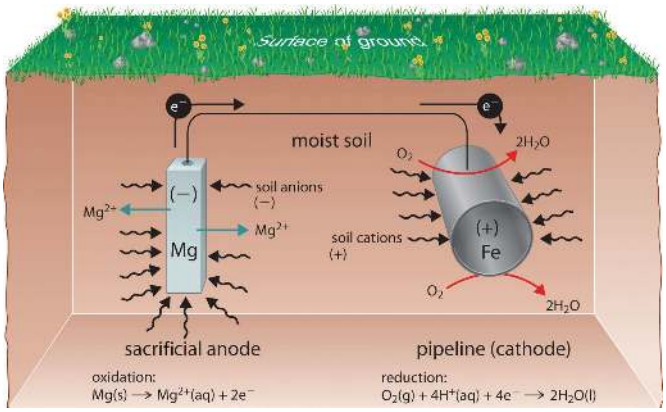


Figure 20.9.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic 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 20.9.1

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 $E^{oo}{}_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E^{oo}{}_{cell}$, 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 $E^{oo}{}_{cell}$.
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:

cathode:	$O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	$E^\circ_{cathode} = 1.23$ V
anode:	$Fe(s) \rightarrow Fe^{2+} + 2e^-$	$E^\circ_{anode} = -0.45$ V
overall:	$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$	$E^\circ_{overall} = 1.68$ V

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 20.9.5).



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 20.9.1

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

Not unless you plan to sell the house very soon because the $\mathrm{Cu/Fe}$ pipe joints will lead to rapid corrosion.

Answer b

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.

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.

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CHAPTER OVERVIEW

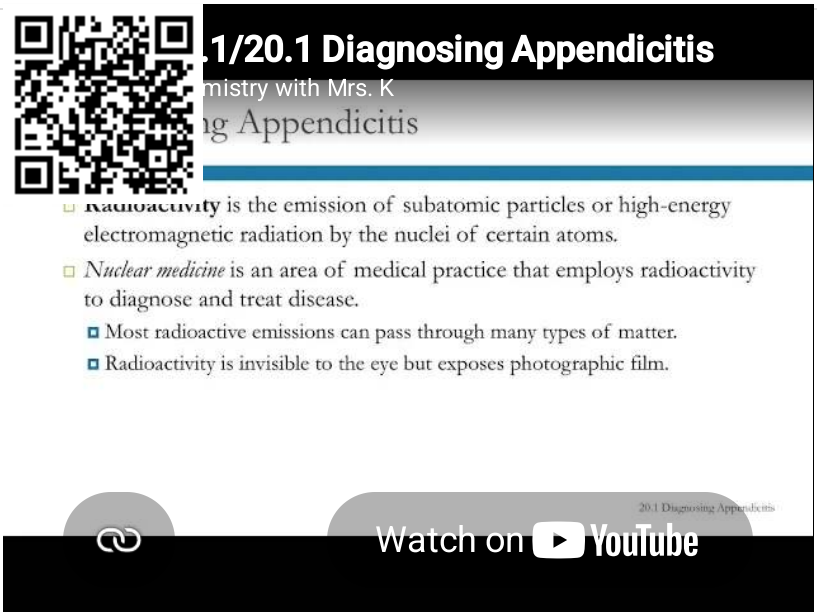
21: Radioactivity and Nuclear Chemistry

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- 21.2: The Discovery of Radioactivity
- 21.3: Types of Radioactivity
- 21.4: The Valley of Stability- Predicting the Type of Radioactivity
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- 21.10: Nuclear Transmutation and Transuranium Elements
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- 21.12: Radioactivity in Medicine and Other Applications

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21.1: Diagnosing Appendicitis



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21.2: The Discovery of Radioactivity

Learning Objectives

- List the most common emissions from naturally radioactive nuclei.
- Compare the energy released per gram of matter in nuclear reactions to that in chemical reactions.
- Express the relationship between nuclear stability and the nuclei's binding energy per nucleon ratio.

No one could have known in the 1800's that the discovery of the fascinating science and art form of photography would eventually lead to the splitting of the atom. The basis of photography is the fact that visible light causes certain chemical reactions. If the chemicals are spread thinly on a surface but protected from light by a covering, no reaction occurs. When the covering is removed, however, light acting on the chemicals causes them to darken. With millions of cameras in use today, we do not think of it as a strange phenomenon—but at the time of its discovery, photography was a strange and wonderful thing.

Even stranger was the discovery by Wilhelm Roentgen—that radiation other than visible light could expose photographic film. He found that film wrapped in dark paper would react when x-rays went through the paper and struck the film.



Figure 21.2.1: Image of Becquerel's photographic plate, which has been fogged by exposure to radiation from a uranium salt. The shadow of a metal Maltese Cross placed between the plate and the uranium salt is clearly visible (Public Domain).

When Henri Becquerel heard about Roentgen's discovery, he wondered if his fluorescent minerals would give the same x-rays. Becquerel placed some of his rock crystals on top of a well-covered photographic plate and sat them in the sunlight. The sunlight made the crystals glow with a bright fluorescent light, but when Becquerel developed the film he was very disappointed. He found that only one of his minerals, a uranium salt, had fogged the photographic plate. He decided to try again, and this time, to leave them out in the sun for a longer period of time. Fortunately, the weather didn't cooperate, and Becquerel had to leave the crystals and film stored in a drawer for several cloudy days. Before continuing his experiments, Becquerel decided to check one of the photographic plates to make sure the chemicals were still good. To his amazement, he found that the plate had been exposed in spots where it had been near the uranium containing rocks, and some of these rocks had not been exposed to sunlight at all. In later experiments, Becquerel confirmed that the radiation from the uranium had no connection with light or fluorescence, but the amount of radiation was directly proportional to the concentration of uranium in the rock. Becquerel had discovered **radioactivity**.

The Curies and Radium

One of Becquerel's assistants, a young Polish scientist named Maria Sklowdowska (to become Marie Curie after she married Pierre Curie), became interested in the phenomenon of radioactivity. With her husband, she decided to find out if chemicals other than uranium were radioactive. The Austrian government was happy to send the Curies a ton of pitchblende from the mining region of Joachimstahl, because it was waste material that had to be disposed of anyway. The Curies wanted the pitchblende because it was the residue of uranium mining. From the ton of pitchblende, the Curies separated $0.10\ \text{g}$ of a previously unknown element, radium, in the form of the compound radium chloride. This radium was many times more radioactive than uranium.

By 1902, the world was aware of a new phenomenon called radioactivity and of new elements which exhibited natural radioactivity. For this work, Becquerel and the Curies shared the 1903 Nobel Prize and for subsequent work; Marie Cure received a second Nobel Prize in 1911. She is the only person ever to receive two Nobel Prizes in science.

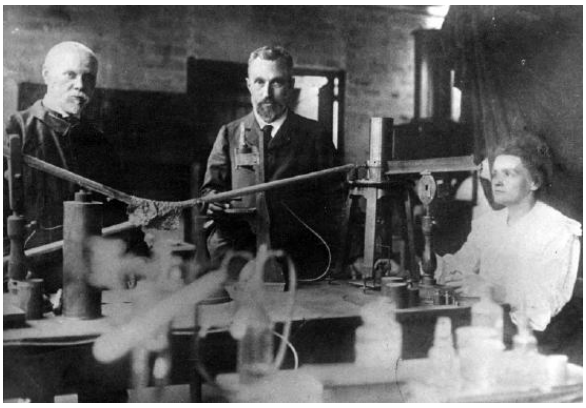


Figure 21.2.2: Marie Curie (right) and Pierre Curie (middle) with Henri Becquerel (left) shared the 1903 Nobel Prize.

Further experiments provided information about the characteristics of the penetrating emissions from radioactive substances. It was soon discovered that there were three common types of radioactive emissions. Some of the radiation could pass easily through aluminum foil while some of the radiation was stopped by the foil. Some of the radiation could even pass through foil up to a centimeter thick. The three basic types of radiation were named alpha, beta, and gamma radiation. The actual composition of the three types of radiation was still not known.

Eventually, scientists were able to demonstrate experimentally that the alpha particle, α, was a helium nucleus (a particle containing two protons and two neutrons), a beta particle, β, was a high speed electron, and gamma rays, γ, were a very high energy form of light (even higher energy than x-rays).

Unstable Nuclei May Disintegrate

A nucleus (with one exception, hydrogen-1) consists of some number of protons and neutrons pulled together in an extremely tiny volume. Since protons are positively charged and like charges repel, it is clear that protons cannot remain together in the nucleus unless there is a powerful force holding them there. The force which holds the nucleus together is generated by **nuclear binding energy**.

A nucleus with a large amount of binding energy per nucleon (proton or neutron) will be held together tightly and is referred to as stable. These nuclei do not break apart. When there is too little binding energy per nucleon, the nucleus will be less stable and may disintegrate (come apart). Such disintegration is referred to as **natural radioactivity**. It is also possible for scientists to smash nuclear particles together and cause nuclear reactions between normally stable nuclei. This disintegration is referred to as **artificial radioactivity**. None of the elements above #92 on the periodic table occur on earth naturally—they are all products of artificial (manmade) radioactivity.

When nuclei come apart, they come apart violently accompanied by a tremendous release of energy in the form of heat, light, and radiation. This energy comes from some of the nuclear binding energy. In nuclear changes, the energy involved comes from the nuclear binding energy. However, in chemical reactions, the energy comes from electrons moving energy levels. A typical nuclear change (such as fission) may involve millions of times more energy per atom changing compared to a chemical change (such as burning)!

Summary

- Henri Becquerel, Marie Curie, and Pierre Curie shared the discovery of radioactivity.

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21.3: Types of 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:

$$^{A}_{Z}\mathrm{X} \tag{21.3.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $^{14}_{6}\mathrm{C}$ is called "carbon-14."

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^6 meters, 30,000 times larger).

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Nuclear Equations

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}\mathrm{O}$ is a product of the nuclear reaction of $^{14}_{7}\mathrm{N}$ and $^{4}_{2}\mathrm{He}$ if we knew that a proton, $^{1}_{1}\mathrm{H}$, was one of the two products. Example $21.3.1$ shows how we can identify a nuclide by balancing the nuclear reaction.

Example 21.3.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 ($^{25}_{12}\mathrm{Mg}$) produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X}$$

where

- A is the mass number and
- Z is the atomic number of the new nuclide, X.

Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = \mathrm{A} + 1$$

so

$$\mathrm{A} = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = \mathrm{Z} + 1$$

so

$$\mathrm{Z} = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\mathrm{Al}$.

Exercise 21.3.1

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

$$^{125}_{53}\mathrm{I} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{125}_{52}\mathrm{Te}$$

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

> *Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.*

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of

either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the ${}^{A}_{Z}\mathrm{X}$ notation for nuclides to include radioactive emissions. Table 21.3.1 lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

Table 21.3.1: Nuclear Decay Emissions and Their Symbols

Identity	Symbol	Charge	Mass (amu)
helium nucleus	${}^{4}_{2}\alpha$	+2	4.001506
electron	${}^{0}_{-1}\beta$ or β^{-}	−1	0.000549
photon	${}^{0}_{0}\gamma$	—	—
neutron	${}^{1}_{0}\mathrm{n}$	0	1.008665
proton	${}^{1}_{1}\mathrm{p}$	+1	1.007276
positron	${}^{0}_{+1}\beta$ or β^{+}	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = −1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol ${}^{0}_{-1}\mathrm{e}$, which is usually simplified to e^{-}, represents a free electron or an electron associated with an atom, whereas the symbol ${}^{0}_{-1}\beta$, which is often simplified to β^{-}, denotes an electron that originates from within the nucleus, which is a β particle. Similarly, ${}^{4}_{2}\mathrm{He}^{2+}$ refers to the nucleus of a helium atom, and ${}^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 21.3.1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.

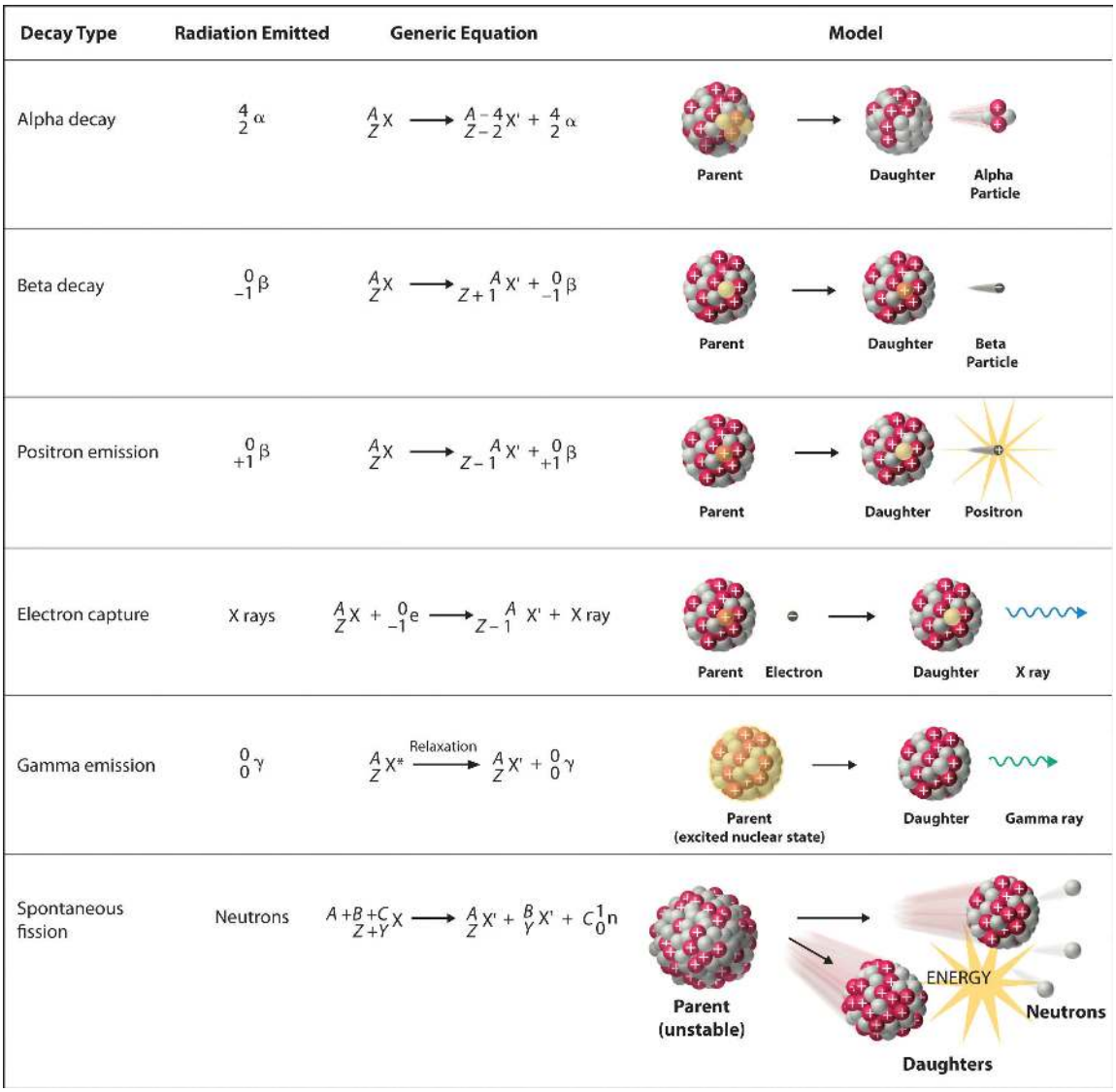


Figure 21.3.1: Common Modes of Nuclear Decay

The different types of decay are alpha, beta, positron emission, electron capture, gamma emission, and spontaneous fission.

Alpha α Decay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, ${}^{4}_{2}\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\\text{particle}}}{{}^{4}_{2}\alpha} \tag{21.3.2}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha \tag{21.3.3}$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

> *Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.*

Beta β^- Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\\text{neutron in}\\\text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\\text{retained}\\\text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\\text{emitted by}\\\text{nucleus}}}{{}^{0}_{-1}\beta} \tag{21.3.4}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{21.3.5}$$

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:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta$$

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:

$${}^{1}_{1}\text{p}^{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta^{+} \tag{21.3.6}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \underset{\text{positron}}{{}^{0}_{+1}\beta^{+}}$$

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:

$${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta^{+}$$

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:

$${}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n} \tag{21.3.7}$$

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

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} + \underset{\text{electron}}{{}^{0}_{-1}\text{e}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \text{x-ray}$$

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:

$$^{55}_{26}\text{Fe} \xrightarrow{\text{EC}} {}^{55}_{25}\text{Mn} + \text{x-ray}$$

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:

$$^{55}_{26}\text{Fe} + {}^{0}_{-1}\text{e} \rightarrow {}^{55}_{25}\text{Mn} + \text{x-ray}$$

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:

$$^{238}_{92}\text{U} \rightarrow \underbrace{^{234}_{90}\text{Th}^*}_{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\text{Th}^* \rightarrow {}^{234}_{88}\text{Th} + {}^{0}_{0}\gamma$$

or more generally,

$$^{A}_{Z}\text{X}^* \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{0}\gamma$$

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 $^{254}_{98}\text{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\text{Cf} \rightarrow {}^{118}_{46}\text{Pd} + {}^{132}_{52}\text{Te} + 4{}^{1}_{0}\text{n}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

Example 21.3.2

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\mathrm{S}$
b. the decay of $^{201}_{80}\mathrm{Hg}$ by electron capture
c. the decay of $^{30}_{15}\mathrm{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as $^{A}_{Z}\mathrm{X}$:

$$^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta$$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta$$

b.

A We know the identities of both reactants: $^{201}_{80}\mathrm{Hg}$ and an inner electron, $^{0}_{-1}\mathrm{e}$. The reaction is as follows:

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z}\mathrm{X}$$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{201}_{79}\mathrm{Au}$$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$^{30}_{15}\mathrm{P} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{+1}\beta$$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta$$

Exercise 21.3.2

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

$^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$

Answer d

$^{99}_{42}\mathrm{Mo} \rightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\beta$

Answer c

$^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

Example 21.3.3

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\mathrm{Ti}$
b. $^{242}_{94}\mathrm{Pu}$
c. $^{12}_{5}\mathrm{B}$
d. $^{256}_{100}\mathrm{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise 21.3.3

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

beta decay

Answer d

positron emission or electron capture

Answer c

alpha decay

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases Z by only 2, and positron emission or electron capture decreases Z by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 21.3.2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of "only" 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

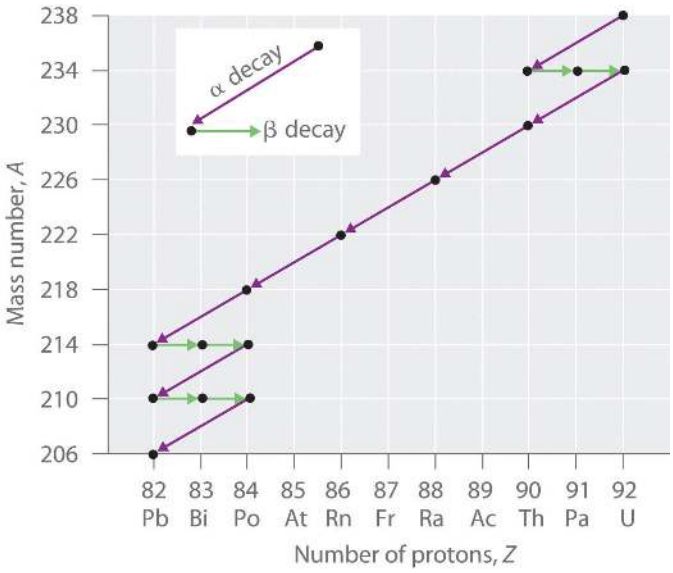


Figure 21.3.2 A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.

Graph of mass number against number of protons. The purple lines are alpha decay which are linear while the green lines are beta decay and are horizontal and parallel to the x axis.

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin.

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p}$$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles neutrons and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{21.3.8}$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 21.3.3). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{21.3.9}$$

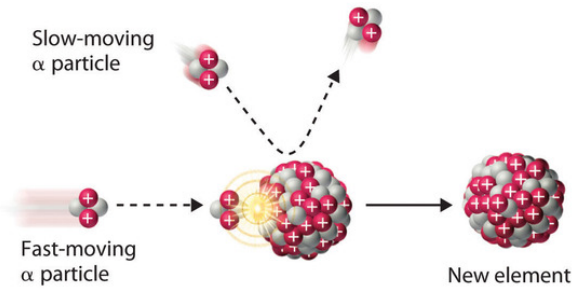


Figure 21.3.3: A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.

Example 21.3.4

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of *Z* and *A* of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum (Z = 13) will be converted to phosphorus (Z = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $^{30}_{15}\mathrm{P}$.

B The balanced nuclear equation for the reaction is as follows:

$$^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n}$$

Exercise 21.3.4

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

neutron, $^{1}_{0}\mathrm{n}$; $^{96}_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{97}_{43}\mathrm{Tc} + {}^{1}_{0}\mathrm{n}$:

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium (Z = 92) and plutonium (Z = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as $^{235}_{92}\mathrm{U}$ and $^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 21.3.4:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{21.3.10}$$

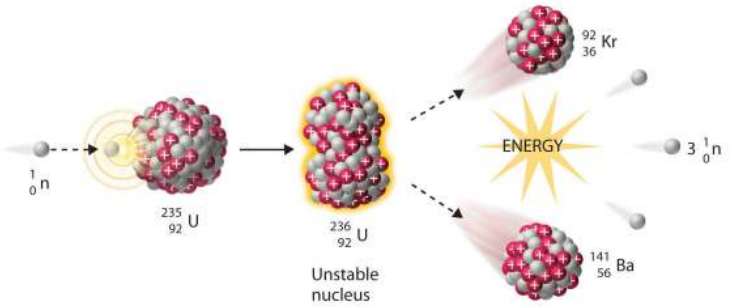


Figure 21.3.4 Neutron-Induced Nuclear Fission. Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a **fissile isotope**.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 21.3.4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 21.3.5, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

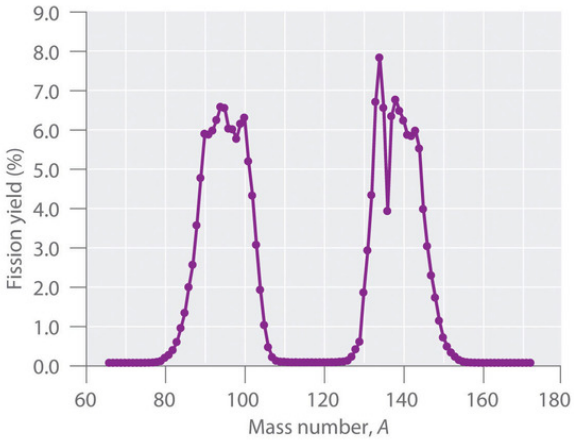


Figure 21.3.5: Mass Distribution of Nuclear Fission Products of ^{235}U. Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for^{235}U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 21.3.2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table 21.3.2: Some Reactions Used to Synthesize Transuranium Elements

$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}\mathrm{Am} + {}^{1}_{1}\mathrm{p} + {}^{1}_{0}\mathrm{n}$
$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}\mathrm{Bk} + {}^{1}_{1}\mathrm{p} + 2{}^{1}_{0}\mathrm{n}$
$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
$^{238}_{92}\mathrm{U} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{246}_{98}\mathrm{Cf} + 4{}^{1}_{0}\mathrm{n}$
$^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{256}_{103}\mathrm{Lr} + 6{}^{1}_{0}\mathrm{n}$

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 21.3.6), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

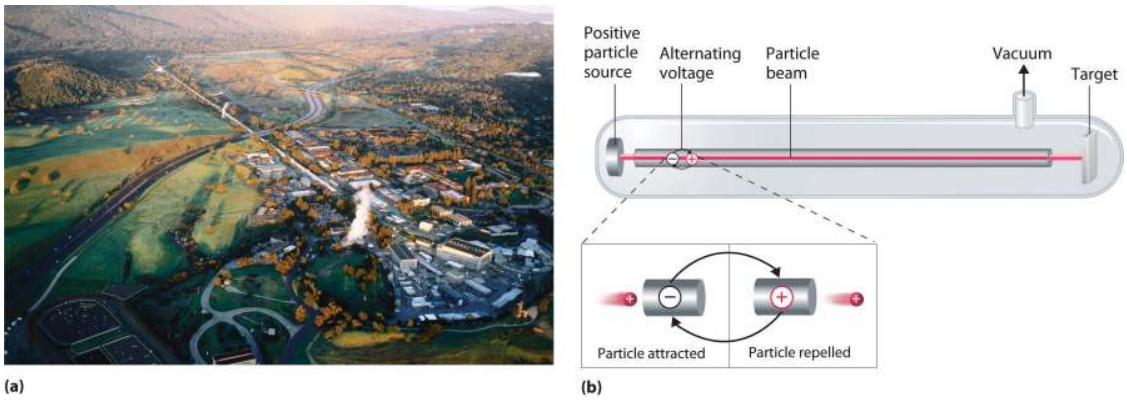


Figure 21.3.6: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as 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

$$^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma$$

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21.4: The Valley of Stability- Predicting the Type of Radioactivity

Learning Objectives

- To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or decay, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

Each element can be represented by the notation ${}^{A}_{Z}\mathrm{X}$, where *A*, the mass number, is the sum of the number of protons and the number of neutrons, and *Z*, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called **nucleons**, and an atom with a particular number of protons and neutrons is called a **nuclide**. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

stable isotopes of oxygen represented in different ways

${}^{A}_{Z}\mathrm{X}$	${}^{16}_{8}\mathrm{O}$	${}^{17}_{8}\mathrm{O}$	${}^{18}_{8}\mathrm{O}$
${}^{A}\mathrm{X}$	${}^{16}\mathrm{O}$	${}^{17}\mathrm{O}$	${}^{18}\mathrm{O}$
element-A:	oxygen-16	oxygen-17	oxygen-18

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17. Any nucleus that is unstable and decays spontaneously is said to be **radioactive**, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called **radioisotopes**.

Nuclear Stability

The nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the **strong nuclear force**, an extremely powerful but very short-range attractive force between nucleons (Figure 21.4.1). All stable nuclei except the hydrogen-1 nucleus (${}^{1}\mathrm{H}$) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

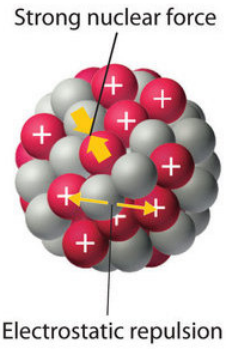


Figure 21.4.1: Competing Interactions within the Atomic Nucleus. Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 21.4.2. The stable isotopes form a “peninsula of stability” in a “sea of instability.” Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., $^{4}_{2}\mathrm{He}$, $^{10}_{5}\mathrm{B}$, and $^{40}_{20}\mathrm{Ca}$). All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with Z > 83 are unstable and radioactive.

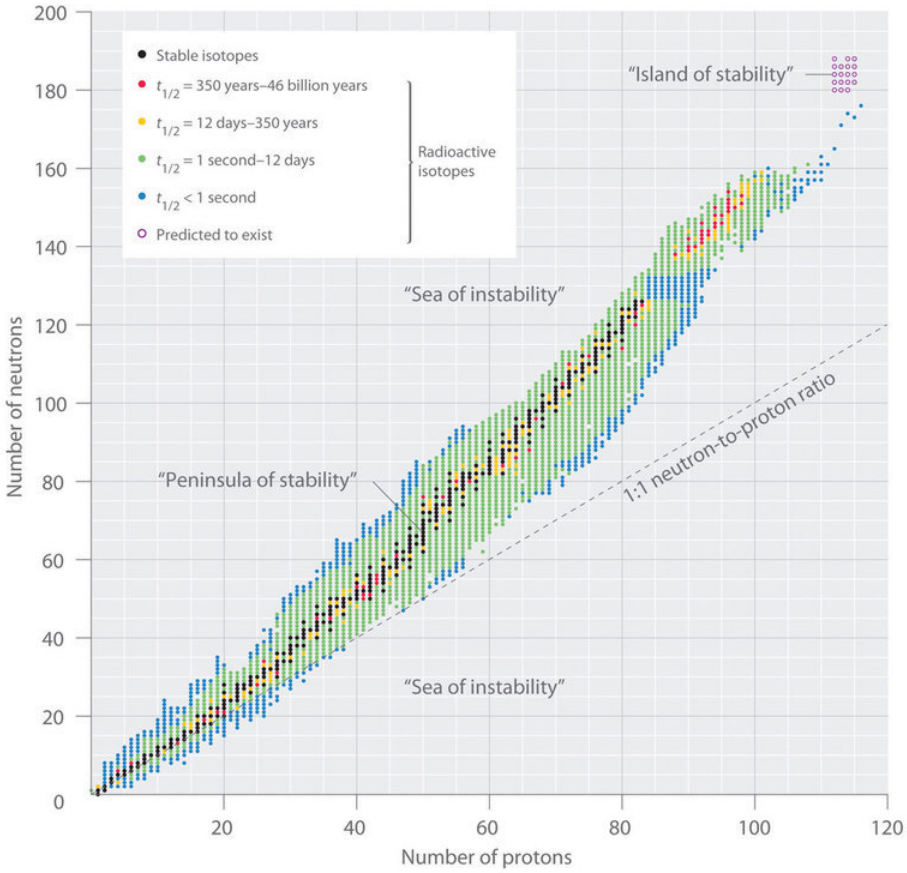


Figure 21.4.2: The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio. In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized. Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart.

Graph of number or neutrons against the number or protons. The graph is divided into sections of "sea of instability", "peninsula of stability", "sea of instability" and "island of stability"

As shown in Figure 21.4.3, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin (Z = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium (Z = 49) and antimony (Z = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be “doubly magic” and are even more stable. Examples of elements with doubly magic nuclei are $^{4}_{2}\mathrm{He}$, with 2 protons and 2 neutrons, and $^{208}_{82}\mathrm{Pb}$, with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

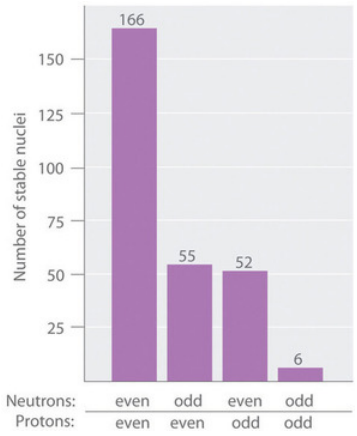


Figure 21.4.3: The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability.

> *Most stable nuclei contain **even** numbers of both neutrons and protons*

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 21.4.2, the "peninsula" of stable isotopes is surrounded by a "reef" of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

Origin of the Magic Numbers

Multiple models have been formulated to explain the origin of the magic numbers and two popular ones are the Nuclear Shell Model and the Liquid Drop Model. Unfortuneatly, both require advanced quantum mechanics to fully understand and are beyond the scope of this text.

Example 21.4.1

Classify each nuclide as stable or radioactive.

a. $^{30}_{15}\mathrm{P}$
b. $^{98}_{43}\mathrm{Tc}$
c. tin-118
d. $^{239}_{94}\mathrm{Pu}$

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

a. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 21.4.2, its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $^{30}_{15}\mathrm{P}$ is predicted to be radioactive, and it is.

b. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $^{98}_{43}\mathrm{Tc}$ near the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are

unstable. These facts suggest that $^{98}_{43}\mathrm{Tc}$ might be stable. However, $^{98}_{43}\mathrm{Tc}$ has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $^{98}_{43}\mathrm{Tc}$ is predicted to be radioactive, and it is.

c. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an even number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus $^{118}_{50}\mathrm{Sn}$should be particularly stable.

d. This nuclide has an atomic number of 94. Because all nuclei with Z > 83 are unstable, $^{239}_{94}\mathrm{Pu}$ must be radioactive.

? Exercise 21.4.1

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

Answer b

stable

Answer c

radioactive

Answer 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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21.5: Detecting Radioactivity

Learning Objectives

- Understand how the Geiger counter can be used to quantify the rate of ionization radiation.

When alpha, beta or gamma particles collide with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*. Alpha, beta and gamma radiation are broadly referred to as **ionizing radiation**. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this in order to detect these particles. In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry. Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter. A simple schematic of a Geiger counter is shown in Figure 21.5.1.

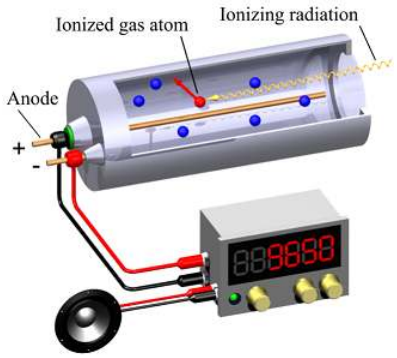


Figure 21.5.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia(opens in new window)).

Although scientists were not aware at the time of the Geiger counter's invention, all of us are subjected to a certain amount of radiation every day. This radiation is called **background radiation** and comes from a variety of natural and artificial radiation sources. Approximately 82% of background radiation comes from natural sources. These natural sources include:

1. Sources in the earth—including naturally occurring radioactive elements—which are incorporated in building materials, and also in the human body.
2. Sources from space in the form of cosmic rays.
3. Sources in the atmosphere, such as radioactive radon gas released from the earth; and radioactive atoms like carbon-14, produced in the atmosphere by bombardment from high-energy cosmic rays.

Measuring Radiation Exposure

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21.6: The Kinetics of Radioactive Decay and Radiometric Dating

Learning Objectives

- To know how to use half-lives to describe the rates of first-order reactions

Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value. This period of time is called the **half-life** of the reaction, written as $t_{1/2}$. Thus the half-life of a reaction is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_{0/2}$. If two reactions have the same order, the faster reaction will have a shorter half-life, and the slower reaction will have a longer half-life.

The half-life of a first-order reaction under a given set of reaction conditions is a constant. This is not true for zeroth- and second-order reactions. The half-life of a first-order reaction is independent of the concentration of the reactants. This becomes evident when we rearrange the integrated rate law for a first-order reaction to produce the following equation:

$$\ln \frac{[A]_0}{[A]} = kt \tag{21.6.1}$$

Substituting $[A]_{0/2}$ for $[A]$ and $t_{1/2}$ for t (to indicate a half-life) into Equation 21.6.1 gives

$$\ln \frac{[A]_0}{[A]_0/2} = \ln 2 = kt_{1/2} \tag{21.6.2}$$

Substituting $\ln 2 \approx 0.693$ into the equation results in the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \tag{21.6.3}$$

Thus, for a first-order reaction, each successive half-life is the same length of time, as shown in Figure 21.6.1, and is *independent* of $[A]$.

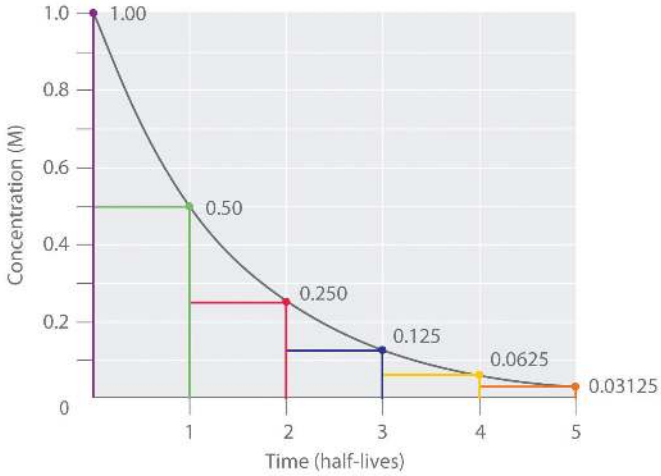


Figure 21.6.1: The Half-Life of a First-Order Reaction. This plot shows the concentration of the reactant in a first-order reaction as a function of time and identifies a series of half-lives, intervals in which the reactant concentration decreases by a factor of 2. In a first-order reaction, every half-life is the same length of time.

If we know the rate constant for a first-order reaction, then we can use half-lives to predict how much time is needed for the reaction to reach a certain percent completion.

Number of Half-Lives	Percentage of Reactant Remaining	
1	$\frac{100\%}{2} = 50\%$	$\frac{1}{2}(100\%) = 50\%$
2	$\frac{50\%}{2} = 25\%$	$\frac{1}{2}\left(\frac{1}{2}\right)(100\%) = 25\%$
3	$\frac{25\%}{2} = 12.5\%$	$\frac{1}{2}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(100\%) = 12.5\%$
n	$\frac{100\%}{2^n}$	$\left(\frac{1}{2}\right)^n(100\%) = \left(\frac{1}{2}\right)^n\%$

As you can see from this table, the amount of reactant left after n half-lives of a first-order reaction is $(1/2)^n$ times the initial concentration.

> *For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of [A].*

Example 21.6.1

The anticancer drug cis-platin hydrolyzes in water with a rate constant of 1.5×10^{-3} min^{-1} at pH 7.0 and 25°C. Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cis-platin has a concentration of 0.053 M, what will be the concentration of cis-platin after 5 half-lives? after 10 half-lives? What is the percent completion of the reaction after 5 half-lives? after 10 half-lives?

Given: rate constant, initial concentration, and number of half-lives

Asked for: half-life, final concentrations, and percent completion

Strategy:

A. Use Equation 21.6.3 to calculate the half-life of the reaction.
B. Multiply the initial concentration by 1/2 to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.
C. Subtract the remaining concentration from the initial concentration. Then divide by the initial concentration, multiplying the fraction by 100 to obtain the percent completion.

Solution A

We can calculate the half-life of the reaction using Equation 21.6.3:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3}\ \text{min}^{-1}} = 4.6 \times 10^2\ \text{min}$$

Thus it takes almost 8 h for half of the cis-platin to hydrolyze.

Solution B

fter 5 half-lives (about 38 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053\ \text{M}}{2^5} = \frac{0.053\ \text{M}}{32} = 0.0017\ \text{M}$$

After 10 half-lives (77 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053\ \text{M}}{2^{10}} = \frac{0.053\ \text{M}}{1024} = 5.2 \times 10^{-5}\ \text{M}$$

Solution C

The percent completion after 5 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053\ \text{M} - 0.0017\ \text{M})(100)}{0.053} = 97\%$$

The percent completion after 10 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053\ \text{M} - 5.2 \times 10^{-5}\ \text{M})(100)}{0.053\ \text{M}} = 100\%$$

Thus a first-order chemical reaction is 97% complete after 5 half-lives and 100% complete after 10 half-lives.

? Exercise 21.6.1

Ethyl chloride decomposes to ethylene and HCl in a first-order reaction that has a rate constant of $1.6 \times 10^{-6}\ \text{s}^{-1}$ at 650°C.

a. What is the half-life for the reaction under these conditions?
b. If a flask that originally contains 0.077 M ethyl chloride is heated at 650°C, what is the concentration of ethyl chloride after 4 half-lives?

Answer a

4.3×10^5 s = 120 h = 5.0 days;

Answer b

4.8×10^{-3} M

Radioactive Decay Rates

Radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using N to represent the number of atoms of the radioactive isotope, we can define the **rate of decay** of the sample, which is also called its **activity (*A*)** as the decrease in the number of the radioisotope's nuclei per unit time:

$$A = -\frac{\Delta N}{\Delta t} \tag{21.6.4}$$

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm).

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN \tag{21.6.5}$$

Here, the symbol k is the radioactive decay constant, which has units of inverse time (e.g., s^{-1}, yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 21.6.4 and Equation 21.6.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{\Delta N}{\Delta t} = kN \tag{21.6.6}$$

Equation 21.6.6 is the same as the equation for the reaction rate of a first-order reaction, except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay is a first-order process and can be described in terms of either the differential rate law (Equation 21.6.6) or the integrated rate law:

$$N = N_0 e^{-kt} \tag{21.6.7}$$

$$\ln \frac{N}{N_0} = -kt \tag{21.6.8}$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the half-life of the isotope. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter

half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 14.6, along with some of their applications.

Table 21.6.2: Half-Lives and Applications of Some Radioactive Isotopes

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99*m**	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth's crust
americium-241	432.2 yr	smoke detectors

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Note

Radioactive decay is a first-order process.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth's atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}\mathrm{C}\ {}^{14}\mathrm{N} + \beta^- \rightarrow \tag{21.6.9}$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g of carbon (Figure 21.6.2). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables

scientists to estimate the age of the artifact, as illustrated in Example 11.Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

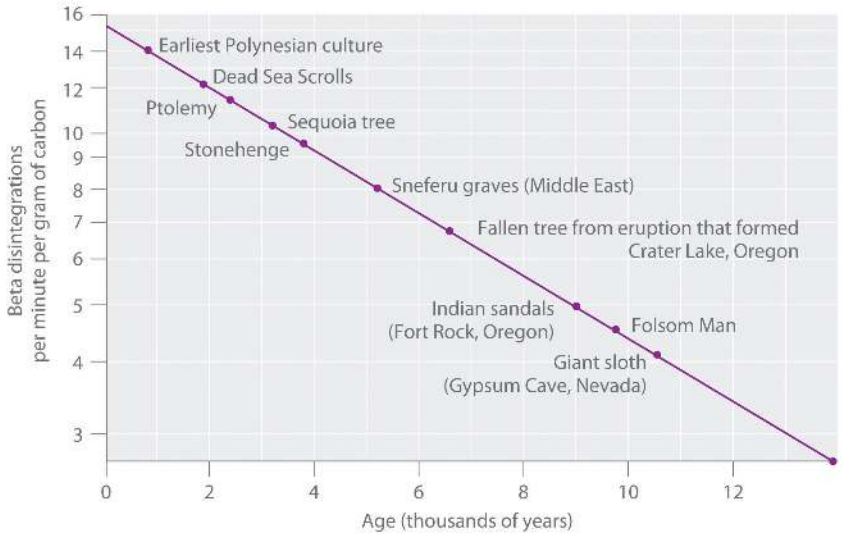


Figure 21.6.2: Radiocarbon Dating. A plot of the specific activity of ^{14}C versus age for a number of archaeological samples shows an inverse linear relationship between ^{14}C content (a log scale) and age (a linear scale).

Example 21.6.2

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the ^{14}C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

Given: isotope and final activity

Asked for: elapsed time

Strategy: Step A

Use Equation 21.6.5 to calculate N_0/N. Then substitute the value for the half-life of ^{14}C into Equation 21.6.3 to find the rate constant for the reaction.

Strategy: Step B

Using the values obtained for N_0/N and the rate constant, solve Equation 21.6.8 to obtain the elapsed time.

Solution

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 21.6.8) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$\ln \frac{N}{N_0} = -kt \tag{21.6.10}$$

$$\frac{\ln(N_0/N)}{k} = t \tag{21.6.11}$$

Step A

From Equation 21.6.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 dpm and A = 8.0 dpm) to calculate N_0/N:

$$\frac{A_0}{A} = \frac{kN_0}{kN} = \frac{N_0}{N} = \frac{15}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 21.6.3:

$$t_{1/2} = \frac{0.693}{k}$$

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ yr}} = 1.22 \times 10^{-4} \text{ yr}^{-1}$$

Step B

Substituting into the equation for *t*,

$$t = \frac{\ln(N_0/N)}{k} = \frac{\ln(15/8.0)}{1.22 \times 10^{-4} \text{ yr}^{-1}} = 5.2 \times 10^3 \text{ yr}$$

From our calculations, the man died 5200 yr ago.

? Exercise 21.6.2

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a ^{14}C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

Answer

30,000 yr

Summary

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$. Radioactive decay reactions are first-order reactions. The rate of decay, or activity, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

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21.7: The Discovery of Fission- The Atomic Bomb and Nuclear Power

Learning Objectives

- Explain nuclear fission
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 21.7.1.

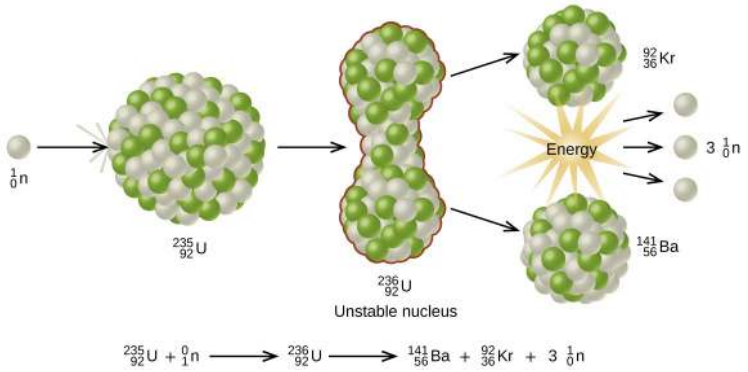


Figure 21.7.1: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 21.7.2. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

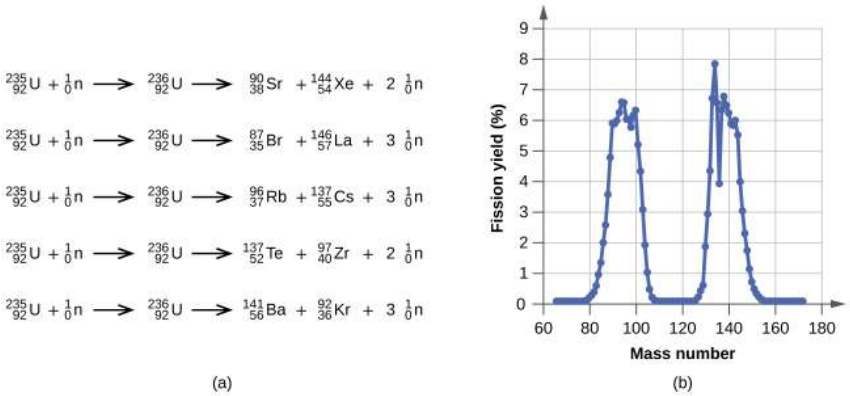


Figure 21.7.2: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two “medium-sized” nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure 21.7.3). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

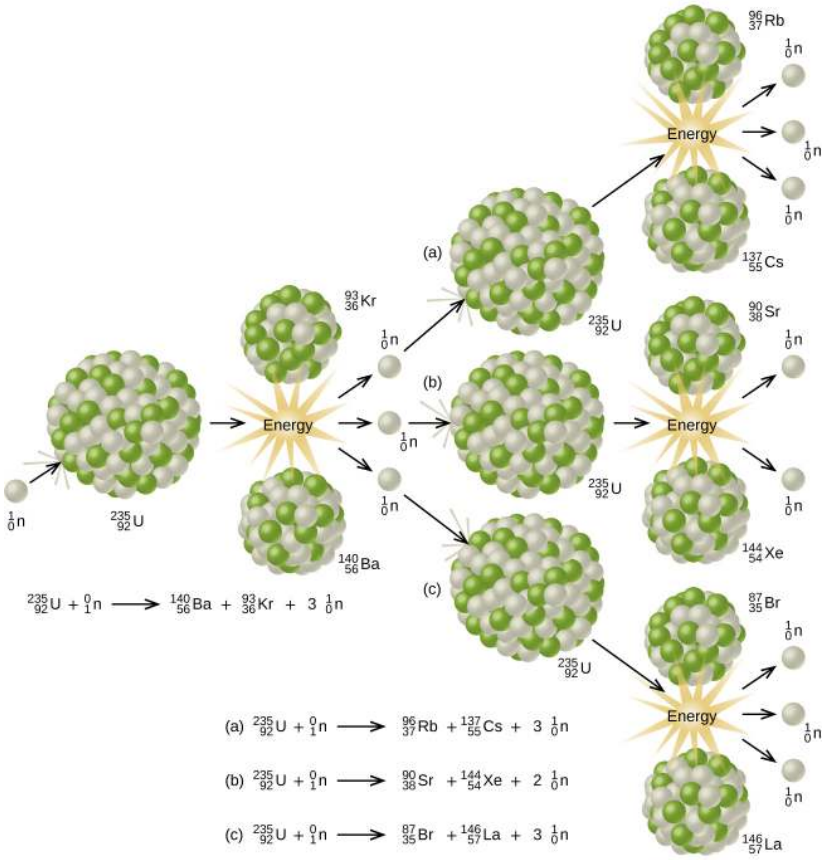


Figure 21.7.3: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 21.7.4).

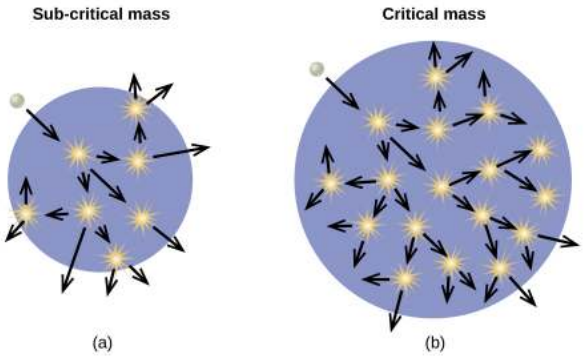


Figure 21.7.4: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 21.7.5) contains several pounds of fissionable material, $^{235}_{92}\mathrm{U}$ or $^{239}_{94}\mathrm{Pu}$, a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the

relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

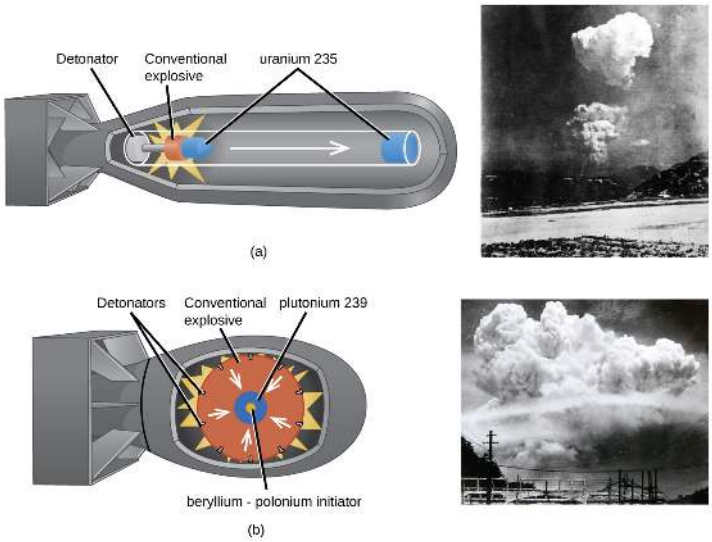


Figure 21.7.5: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a nuclear reactor (Figure 21.7.6). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

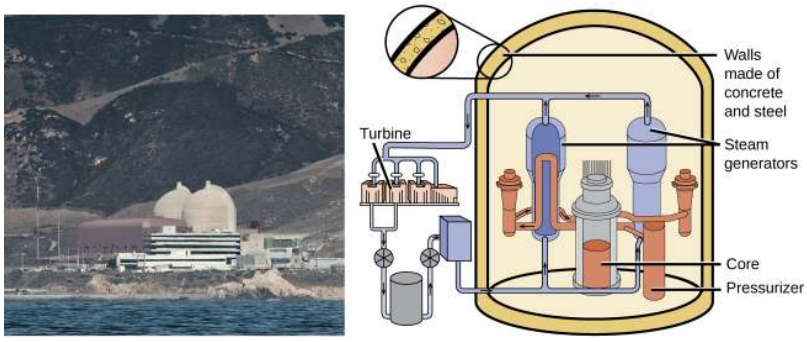


Figure 21.7.6: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass

necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham's law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (Figure 21.7.4). 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 ($^{2}_{1}H_2O$) or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure 21.7.8) 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:

$$^{10}_{5}B + {}^{1}_{0}n \longrightarrow {}^{7}_{3}Li + {}^{4}_{2}He \tag{21.7.1}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

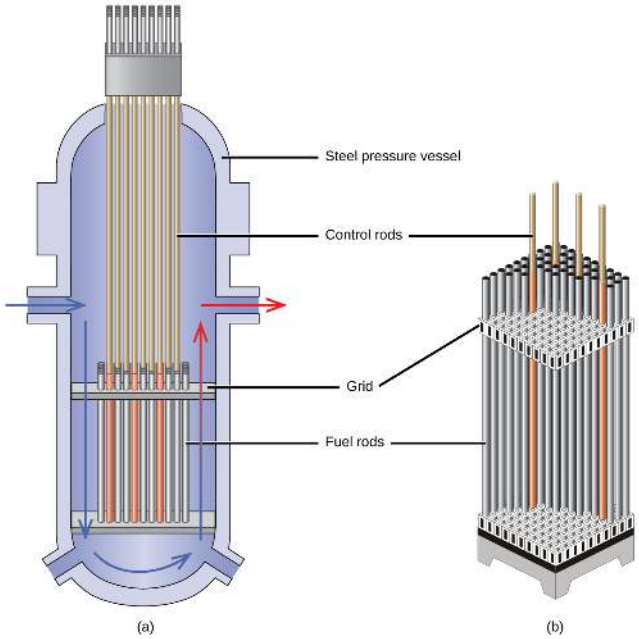


Figure 21.7.7: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, glossary.periodni.com/glossar...en=control+rod)

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.



Video 21.7.1***:*** *Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.*

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g) \tag{21.7.2}$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 21.7.8).

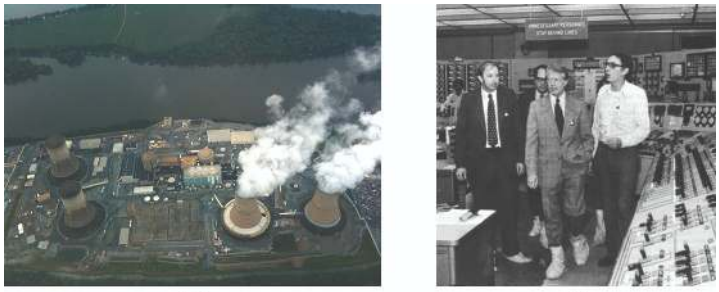


Figure 21.7.8: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 21.7.10).



Figure 21.7.9: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Contributors and Attributions

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21.8: Converting Mass to Energy- Mass Defect and Nuclear Binding Energy

Learning Objectives

- To calculate a mass-energy balance and a nuclear binding energy.
- To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

Mass–Energy Balance

The relationship between mass (m) and energy (E) is expressed in the following equation:

$$E = mc^2 \tag{21.8.1}$$

where

- c is the speed of light ($2.998 \times 10^8\ m/s$), and
- E and m are expressed in units of joules and kilograms, respectively.

Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 21.8.1, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? The solution to this apparent contradiction is that chemical reactions are indeed accompanied by changes in mass, but these changes are simply too small to be detected. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

$$\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -393.5\ \mathrm{kJ/mol} \tag{21.8.2}$$

Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH. When a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE. For most chemical reactions, however, ΔE ≈ ΔH. If we rewrite Einstein's equation as

$$\Delta E = (\Delta m)c^2 \tag{21.8.3}$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2} \tag{21.8.4}$$

Because 1 J = 1 (kg•m^2)/s^2, the change in mass is as follows:

$$\Delta m = \frac{-393.5\ \mathrm{kJ/mol}}{(2.998 \times 10^8\ \mathrm{m/s})^2} = \frac{-3.935 \times 10^5 (\mathrm{kg \cdot m^2})/(\mathrm{s^2 \cdot mol})}{(2.998 \times 10^8\ \mathrm{m/s})^2} = -4.38 \times 10^{-12}\ \mathrm{kg/mol} \tag{21.8.5}$$

This is a mass change of about 3.6 × 10^{-10} g/g carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of ^{14}C to ^{14}N and an electron (a β particle), there is a much larger change in mass:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta \tag{21.8.6}$$

We can use the experimentally measured masses of subatomic particles and common isotopes given in Table 20.1 to calculate the change in mass directly. The reaction involves the conversion of a neutral ^{14}C atom to a positively charged ^{14}N ion (with six, not seven, electrons) and a negatively charged β particle (an electron), so the mass of the products is identical to the mass of a neutral ^{14}N atom. The total change in mass during the reaction is therefore the difference between the mass of a neutral ^{14}N atom (14.003074 amu) and the mass of a ^{14}C atom (14.003242 amu):

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \tag{21.8.7}$$
$$= 14.003074 \text{ amu} - 14.003242 \text{ amu} = -0.000168 \text{ amu} \tag{21.8.8}$$

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:

$$\Delta E = (\Delta m)c^2 = (-1.68 \times 10^{-7} \text{ kg})(2.998 \times 10^{8} \text{ m/s})^2 \tag{21.8.9}$$
$$= -1.51 \times 10^{10} (\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10} \text{ J} = -1.51 \times 10^{7} \text{ kJ} \tag{21.8.10}$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of ^{14}C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = 10^3 eV), megaelectronvolts (1 MeV = 10^6 eV), and even gigaelectronvolts (1 GeV = 10^9 eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of ^{14}C is thus

$$(-1.68 \times 10^{-4} \text{ amu}) \left(\frac{931 \text{ MeV}}{\text{amu}} \right) = -0.156 \text{ MeV} = -156 \text{ keV}$$

Example 21.8.1

Calculate the changes in mass (in atomic mass units) and energy (in joules per mole and electronvolts per atom) that accompany the radioactive decay of ^{238}U to ^{234}Th and an α particle. The α particle absorbs two electrons from the surrounding matter to form a helium atom.

Given: nuclear decay reaction

Asked for: changes in mass and energy

Strategy:

A Use the mass values in Table 20.1 to calculate the change in mass for the decay reaction in atomic mass units.

B Use Equation 21.8.4 to calculate the change in energy in joules per mole.

C Use the relationship between atomic mass units and megaelectronvolts to calculate the change in energy in electronvolts per atom.

Solution

A Using particle and isotope masses from Table 20.1, we can calculate the change in mass as follows:

$$\Delta m = \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} = (\text{mass } ^{234}\text{Th} + \text{mass } {}^{4}_{2}\text{He}) - \text{mass } ^{238}\text{U} \tag{21.8.11}$$
$$= (234.043601 \text{ amu} + 4.002603 \text{ amu}) - 238.050788 \text{ amu} = -0.004584 \text{ amu} \tag{21.8.12}$$

B Thus the change in mass for 1 mol of ^{238}U is −0.004584 g or -4.584×10^{-6} kg. The change in energy in joules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-4.584 \times 10^{-6} \text{ kg})(2.998 \times 10^{8} \text{ m/s})^2 = -4.120 \times 10^{11} \text{ J/mol}$$

C The change in energy in electronvolts per atom is as follows:

$$\Delta E = -4.584 \times 10^{-3} \text{ amu} \times \frac{931 \text{ MeV}}{\text{amu}} \times \frac{1 \times 10^{6} \text{ eV}}{1 \text{ MeV}} = -4.27 \times 10^{6} \text{ eV/atom}$$

? Exercise 21.8.1

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

$\Delta m = -2.0 \times 10^{-5}$ amu; $\Delta E = -1.9 \times 10^6$ kJ/mol = −19 keV/atom

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:

$$m_{^2\mathrm{H}} = m_{\mathrm{neutron}} + m_{\mathrm{proton}} + m_{\mathrm{electron}} \tag{21.8.13}$$

$$= 1.008665 \text{ amu} + 1.007276 \text{ amu} + 0.000549 \text{ amu} = 2.016490 \text{ amu} \tag{21.8.14}$$

The difference between the sum of the masses of the components and the measured atomic mass is called the **mass defect** of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 21.8.4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

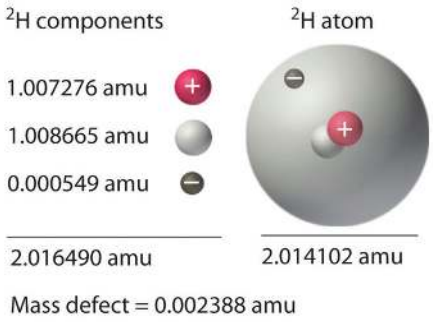


Figure 21.8.1: Nuclear Binding Energy in Deuterium. The mass of a ^{2}H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the **nuclear binding energy** (Figure 21.8.1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

> *Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.*

Not all nuclei are equally stable. Chemists describe the relative stability of different nuclei by comparing the binding energy per nucleon, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 21.8.2, the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

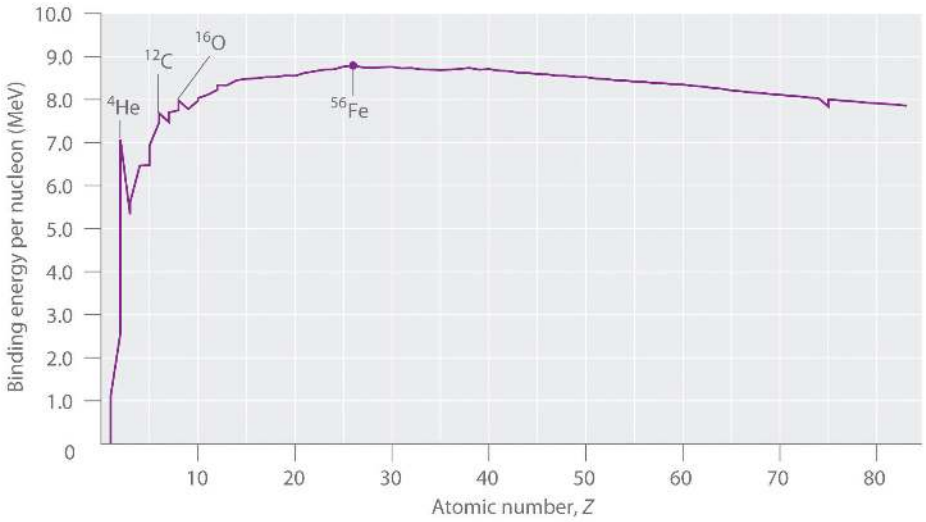


Figure 21.8.2: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Consequently, heavier nuclei (toward the right in Figure 21.8.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 21.8.2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

> *Heavier nuclei spontaneously undergo nuclear reactions that decrease their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that increase their atomic number.*

Example 21.8.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{56}Fe. The experimental mass of the nuclide is given in Table A4.

Given: nuclide and mass

Asked for: nuclear binding energy and binding energy per nucleon

Strategy:

A Sum the masses of the protons, electrons, and neutrons or, alternatively, use the mass of the appropriate number of ^{1}H atoms (because its mass is the same as the mass of one electron and one proton).

B Calculate the mass defect by subtracting the experimental mass from the calculated mass.

C Determine the nuclear binding energy by multiplying the mass defect by the change in energy in electronvolts per atom. Divide this value by the number of nucleons to obtain the binding energy per nucleon.

Solution

A An iron-56 atom has 26 protons, 26 electrons, and 30 neutrons. We could add the masses of these three sets of particles; however, noting that 26 protons and 26 electrons are equivalent to 26 ^{1}H atoms, we can calculate the sum of the masses more quickly as follows:

$$\begin{aligned} \text{calculated mass} &= 26(\text{mass } {}^{1}_{1}\text{H}) + 30(\text{mass } {}^{1}_{0}\text{n}) \\ &= 26(1.007825)\text{amu} + 30(1.008665)\text{amu} = 56.463400 \text{ amu} \\ \text{experimental mass} &= 55.934938 \end{aligned}$$

B We subtract to find the mass defect:

$$\begin{aligned}\text{mass defect} &= \text{calculated mass} - \text{experimental mass} \\ &= 56.463400\ \text{amu} - 55.934938\ \text{amu} = 0.528462\ \text{amu}\end{aligned}$$

C The nuclear binding energy is thus 0.528462 amu × 931 MeV/amu = 492 MeV. The binding energy per nucleon is 492 MeV/56 nucleons = 8.79 MeV/nucleon.

? Exercise 21.8.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{238}U.

Answer

1800 MeV/^{238}U; 7.57 MeV/nucleon

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.

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21.9: Nuclear Fusion - The Power of the Sun

Learning Objectives

- Describe the nuclear reactions in a nuclear fusion reaction
- Quantify the energy released or absorbed in a fusion reaction

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{n} \tag{21.9.1}$$

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:

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n} \tag{21.9.2}$$

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.

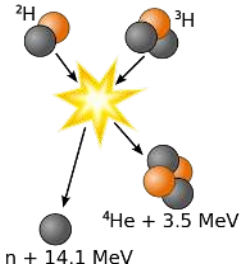


Figure 21.9.1: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of 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 21.9.2).

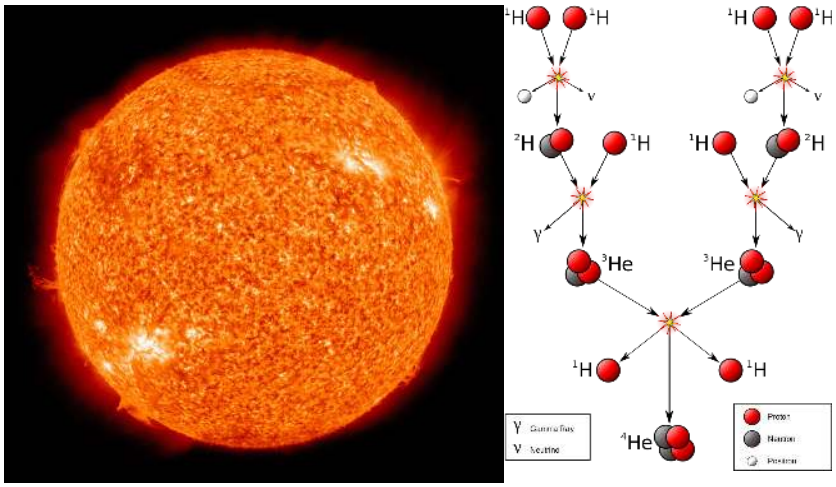


Figure 21.9.2: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 21.9.1

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. $6\,{}^{2}_{1}\mathrm{D} \rightarrow {}^{12}_{6}\mathrm{C}$

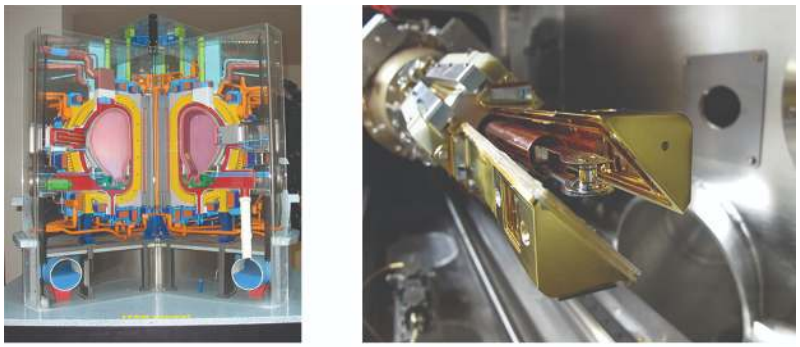
Solution

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.



(a) (b)

Figure 21.9.3: (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 21.9.3). 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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21.10: Nuclear Transmutation and Transuranium Elements

Learning Objectives

- Describe the synthesis of transuranium nuclides

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Science learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{1}_{1}\mathrm{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure 21.10.1). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.



Figure 21.10.1: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2103 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$\begin{aligned} {}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} &\longrightarrow {}^{239}_{92}\mathrm{U} \\ {}^{239}_{92}\mathrm{U} &\longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e} \qquad \text{half-life} = 23.5\ \text{min} \\ {}^{239}_{93}\mathrm{Np} &\longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e} \qquad \text{half-life} = 2.36\ \text{days} \end{aligned}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$${}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu} \tag{21.10.1}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. 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. Some of these elements are shown in Table 21.10.1.

Table 21.10.1: 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	${}^{209}_{83}\mathrm{Bi} + {}^{58}_{26}\mathrm{Fe} \longrightarrow {}^{266}_{109}\mathrm{Mt} + {}^{1}_{0}\mathrm{n}$

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21.11: The Effects of Radiation on Life

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{21.11.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 21.11.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1 \text{ MeV/particle} = 96 \text{ billion J/mol.}$$



Figure 21.11.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue. (CC BY-SA-NC; anonymous)

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time

4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure 21.11.2. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

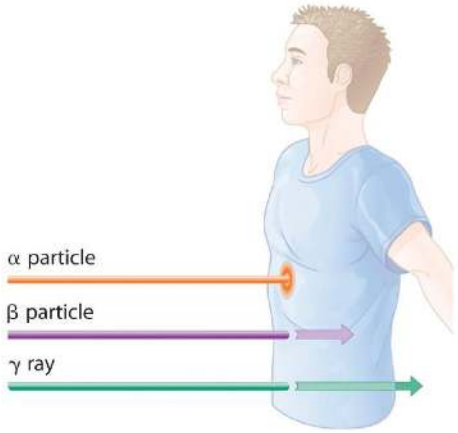


Figure 21.11.2: Depth of Penetration of Ionizing Radiation. The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed. (CC BY-SA-NC; anonymous)

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 21.11.1.

Table 21.11.1: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m

*Distance at which half of the radiation has been absorbed.

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1\ \text{rad} = 0.010\ \text{J/kg} \qquad 1\ \text{Gy} = 1\ \text{J/kg} \tag{21.11.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in man)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 21.11.3). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

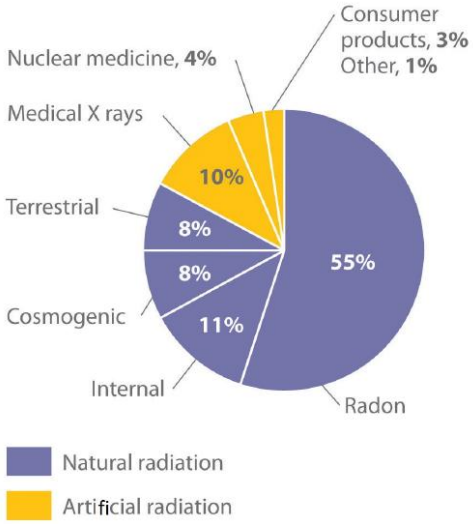


Figure 21.11.3: The Radiation Exposure of a Typical Adult in the United States. The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each. Data source: Office of Civilian Radioactive Waste Management (CC BY-SA-NC; anonymous)

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C:

$$^{14}_{7}\mathrm{N} + {}_{0}^{1}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{21.11.3}$$

The carbon atoms react with oxygen atoms to form CO_2, which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in 1×10^{12} of the carbon atoms in our bodies is radioactive ^{14}C, which decays by beta emission. About 5000 ^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^{3}H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^{3}H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as $^{232}\mathrm{Th}$ and $^{238}\mathrm{U}$ as well as radioactive daughter isotopes, such as$^{226}\mathrm{Ra}$. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% $^{40}\mathrm{K}$, which decays by emitting both a β particle and a (\gamma\) ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 $^{40}\mathrm{K}$ nuclei disintegrated in your body.

By far the most important source of background radiation is radon, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of$^{238}\mathrm{U}$, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, $^{222}\mathrm{Rn}$ undergoes two successive alpha-decay events to give $^{214}\mathrm{Pb}$:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\alpha^{+} + {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\alpha^{+} + {}^{214}_{82}\mathrm{Pb} \tag{21.11.4}$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of $^{218}\mathrm{Po}$ releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The $^{218}\mathrm{Po}$ isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^{3}H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

Example 21.11.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K^+ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05×10^7 decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

A. Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.
B. Determine the number of decays per year for this amount of ^{40}K.
C. Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K:

$$\text{moles } ^{40}\text{K} = 140 \text{ g K} \times \frac{0.0117 \text{ mol } ^{40}\text{K}}{100 \text{ mol K}} \times \frac{1 \text{ mol K}}{40.0 \text{ g K}} = 4.10 \times 10^{-4} \text{ mol } ^{40}\text{K}$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K, so the number of decays per year is as follows:

$$\frac{\text{decays}}{\text{year}} = 4.10 \times 10^{-4} \text{ mol}^{40} \text{ K} \times \frac{1.05 \times 10^7 \text{ decays/s}}{1.00 \text{ mol } ^{40}\text{K}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ yr}}$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$\begin{aligned} \text{total energy per year} &= \frac{1.36 \times 10^{11} \text{ decays}}{\text{yr}} \times \frac{1.32 \text{ MeV}}{\text{decays}} \times \frac{10^6 \text{ eV}}{\text{MeV}} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} \\ &= 2.87 \times 10^{-2} \text{ J/yr} \end{aligned}$$

We use the definition of the rad (1 rad = 10^{-2} J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$\begin{aligned} \text{radiation dose per year} &= \frac{2.87 \times 10^{-2} \text{ J/yr}}{70.0 \text{ kg}} \times \frac{1 \text{ rad}}{1 \times 10^{-2} \text{ J/kg}} \\ &= 4.10 \times 10^{-2} \text{ rad/yr} = 41 \text{ mrad/yr} \end{aligned}$$

This corresponds to almost half of the normal background radiation most people experience.

Exercise 21.11.1

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+}. Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes 4.55×10^{14} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr?

Answer

5.7×10^3 rad/yr (which is 10 times the fatal dose)

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 21.11.2. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 21.11.2: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure 21.11.4, but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

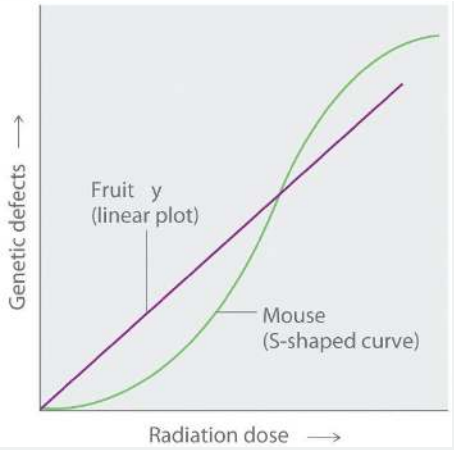


Figure 21.11.4: Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure. Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate. (CC BY-SA-NC; anonymous)

Graph of genetic defects against radiation dose. Fruit is graphed in purple and has a linear plot. Mouse is graphed in green and has a S shaped curve.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include cosmic radiation, consisting of high-energy particles and γ rays emitted by the sun and other stars; cosmogenic radiation, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and terrestrial radiation, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

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21.12: Radioactivity in Medicine and Other Applications

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.

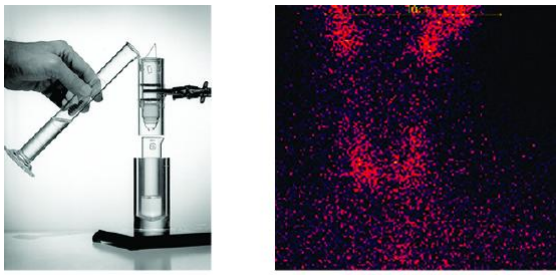
Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), 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 21.12.1) 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 21.12.1: 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 "Blue0ctane"/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 21.12.2). 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.



(a) (b)

Figure 21.12.2: (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 21.12.3). 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.

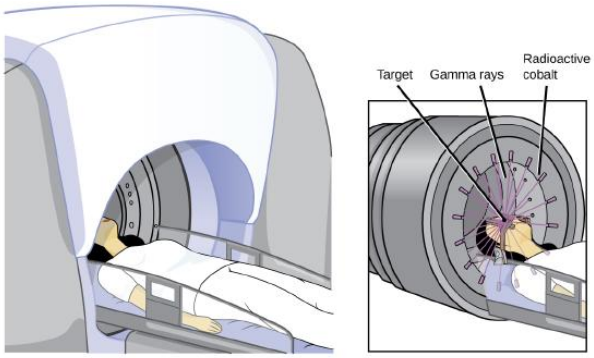


Figure 21.12.3: The cartoon in (a) shows a cobalt-60 machine used in the treatment of cancer. The diagram in (b) shows how the gantry of the Co-60 machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

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 21.12.4.

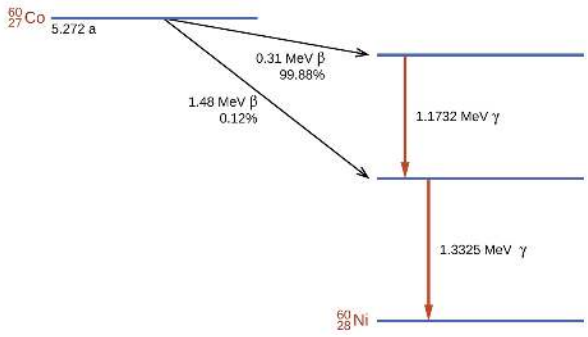


Figure 21.12.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

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:

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g),$$

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 ${}^{14}_{6}C$. 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 21.12.5). 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.

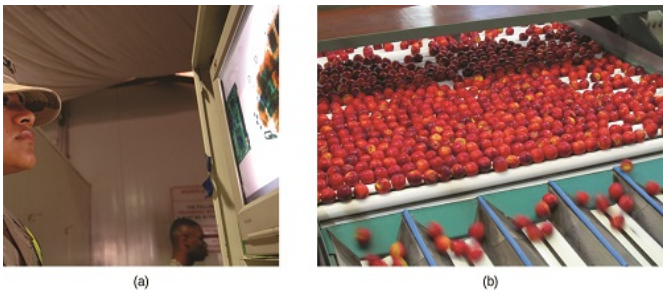


Figure 21.12.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

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 21.12.6). 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.

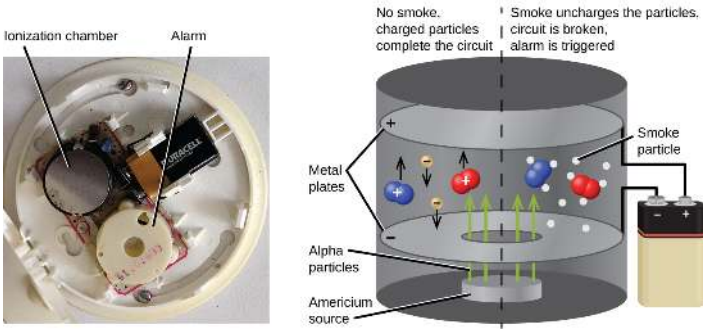


Figure 21.12.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

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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CHAPTER OVERVIEW

22: Organic Chemistry

22.1: Fragrances and Odor
22.2: Hydrocarbons- Compounds Containing Only Carbon and Hydrocarbon
22.3: Polymers
22.4: Alkanes- Saturated Hydrocarbons
22.5: Alkenes and Alkynes
22.6: Hydrocarbon Reactions
22.7: Aromatic Hydrocarbons
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22.11: Carboxylic Acids and Esters
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22.13: Amines

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22.1: Fragrances and Odor



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22.2: Hydrocarbons- Compounds Containing Only Carbon and Hydrocarbon

Learning Objectives

- Identify alkanes, alkenes, alkynes, and aromatic compounds.
- List some properties of hydrocarbons.

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called **hydrocarbons**. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons.

Aliphatic hydrocarbons are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are hydrocarbons that contain at least one C–C double bond, and **Alkynes** are hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called *cycloalkanes* (or *cycloalkenes* or *cycloalkynes*).

Aromatic hydrocarbons have a special six-carbon ring called a *benzene* ring. Electrons in the benzene ring have special energetic properties that give benzene physical and chemical properties that are markedly different from alkanes. Originally, the term *aromatic* was used to describe this class of compounds because they were particularly fragrant. However, in modern chemistry the term *aromatic* denotes the presence of a six-membered ring that imparts different and unique properties to a molecule.

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:

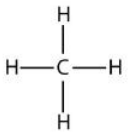


Figure 22.2.1 - Three-Dimensional Representation of Methane.

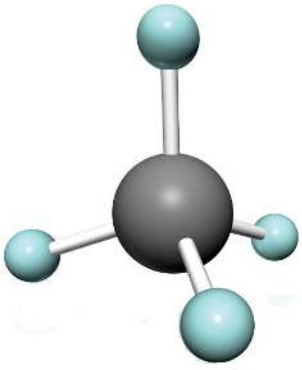
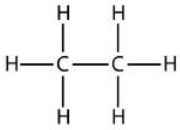
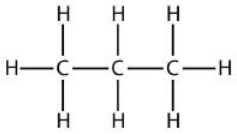


Figure 22.2.1 Three-Dimensional Representation of Methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron.

The next-largest alkane has two C atoms that are covalently bonded to each other. For each C atom to make four covalent bonds, each C atom must be bonded to three H atoms. The resulting molecule, whose formula is C_2H_6, is ethane:



Propane has a backbone of three C atoms surrounded by H atoms. You should be able to verify that the molecular formula for propane is C_3H_8:



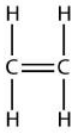
The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule. For example, the condensed structural formula for ethane is CH_3CH_3, while for propane it is $CH_3CH_2CH_3$. Table 22.2.1 - The First 10 Alkanes, gives the molecular formulas, the condensed structural formulas, and the names of the first 10 alkanes.

Table 22.2.1 The First 10 Alkanes

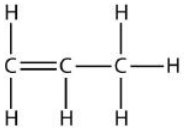
Molecular Formula	Condensed Structural Formula	Name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane

Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Alkenes have a C–C double bond. Because they have less than the maximum number of H atoms possible, they are **unsaturated hydrocarbons**. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:

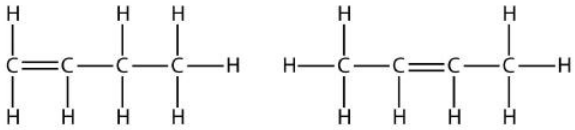


The next largest alkene—propene—has three C atoms with a C–C double bond between two of the C atoms. It is also known as propylene:



What do you notice about the names of alkanes and alkenes? The names of alkenes are the same as their corresponding alkanes except that the ending is *-ene*, rather than *-ane*. Using a stem to indicate the number of C atoms in a molecule and an ending to represent the type of organic compound is common in organic chemistry, as we shall see.

With the introduction of the next alkene, butene, we begin to see a major issue with organic molecules: choices. With four C atoms, the C–C double bond can go between the first and second C atoms or between the second and third C atoms:



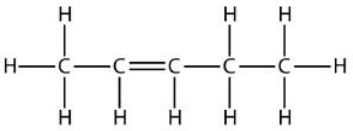
2 structural formulas for butene, with the first butene having the double bond on the first and second carbon from the left and the latter having its double bond on the second and third carbon from the left.

(A double bond between the third and fourth C atoms is the same as having it between the first and second C atoms, only flipped over.) The rules of naming in organic chemistry require that these two substances have different names. The first molecule is named *1-butene*, while the second molecule is named *2-butene*. The number at the beginning of the name indicates where the double bond originates. The lowest possible number is used to number a feature in a molecule; hence, calling the second molecule 3-butene would be incorrect. Numbers are common parts of organic chemical names because they indicate which C atom in a chain contains a distinguishing feature.

The compounds 1-butene and 2-butene have different physical and chemical properties, even though they have the same molecular formula—C_4H_8. Different molecules with the same molecular formula are called **isomers**. Isomers are common in organic chemistry and contribute to its complexity.

Example 22.2.1

Based on the names for the butene molecules, propose a name for this molecule.



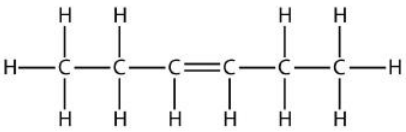
A structural formula of a five carbon molecule with a double bond on the third and fourth carbon from the left. There are ten hydrogen atoms in total.

Solution

With five C atoms, we will use the *pent-* stem, and with a C–C double bond, this is an alkene, so this molecule is a pentene. In numbering the C atoms, we use the number *2* because it is the lower possible label. So this molecule is named 2-pentene.

Exercise 22.2.1

Based on the names for the butene molecules, propose a name for this molecule.



A structural formula of a six carbon molecule with a double bond on the third and fourth carbon from the left. There are twelve hydrogen atoms in total.

Answer

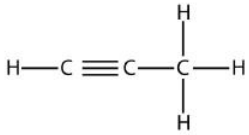
3-hexene

Alkynes, with a C–C triple bond, are named similarly to alkenes except their names end in *-yne*. The smallest alkyne is ethyne, which is also known as acetylene:

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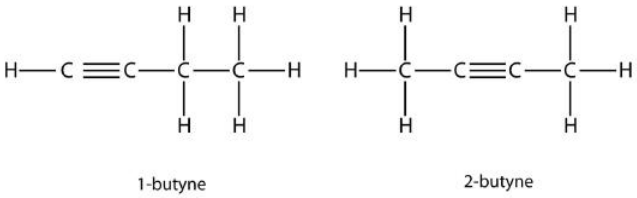


Propyne has the structure



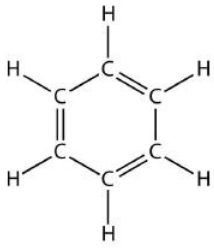
Structural formula showing three carbon molecules with a triple bond present between the first and second carbon atom. The appropriate number of hydrogen atoms is attached to each carbon atom.

With butyne, we need to start numbering the position of the triple bond, just as we did with alkenes:



Two structural formula of butyne. One butyne has a triple bond between the first and second carbon atom, while two butyne has the triple bond between the second and third carbon atom.

Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



The six carbons are arranged in a hexagon pattern with one hydrogen atom emerging outwards from each carbon atom. The presence of a double bond is alternated between every other carbon atom.

The alternating single and double C–C bonds give the benzene ring a special stability, and it does not react like an alkene as might be suspected. Benzene has the molecular formula C_6H_6; in larger aromatic compounds, a different atom replaces one or more of the H atoms.

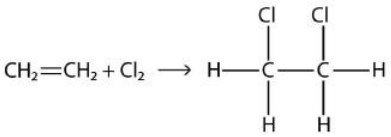
As fundamental as hydrocarbons are to organic chemistry, their properties and chemical reactions are rather mundane. Most hydrocarbons are nonpolar because of the close electronegativities of the C and H atoms. As such, they dissolve only sparingly in H_2O and other polar solvents. Small hydrocarbons, such as methane and ethane, are gases at room temperature, while larger hydrocarbons, such as hexane and octane, are liquids. Even larger hydrocarbons are solids at room temperature and have a soft, waxy consistency.

Hydrocarbons are rather unreactive, but they do participate in some classic chemical reactions. One common reaction is substitution with a halogen atom by combining a hydrocarbon with an elemental halogen. Light is sometimes used to promote the reaction, such as this one between methane and chlorine:

$$CH_4 + Cl_2 \overset{light}{\rightarrow} CH_3Cl + HCl$$

Halogens can also react with alkenes and alkynes, but the reaction is different. In these cases, the halogen reacts with the C–C double or triple bond and inserts itself onto each C atom involved in the multiple bonds. This reaction is called an **addition**

reaction. One example is



Structural formula showing the reaction of ethylene with a chlorine molecule to form ethylene dichloride.

The reaction conditions are usually mild; in many cases, the halogen reacts spontaneously with an alkene or an alkyne.

Hydrogen can also be added across a multiple bond; this reaction is called a **hydrogenation reaction**. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed at a reasonable pace:

$$CH_2 = CH_2 + H_2 \overset{metal\ catalyst}{\rightarrow} CH_3CH_3$$

By far the most common reaction of hydrocarbons is combustion, which is the combination of a hydrocarbon with O_2 to make CO_2 and H_2O. The combustion of hydrocarbons is accompanied by a release of energy and is a primary source of energy production in our society (Figure 22.2.2 - Combustion). The combustion reaction for gasoline, for example, which can be represented by C_8H_{18}, is as follows:

$$2C^8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O + \sim 5060kJ$$



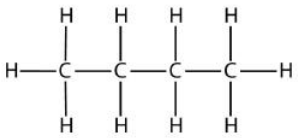
Figure 22.2.2 Combustion © Thinkstock. The combustion of hydrocarbons is a primary source of energy in our society.

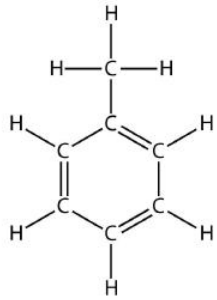
Key Takeaways

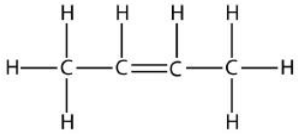
- The simplest organic compounds are hydrocarbons and are composed of carbon and hydrogen.
- Hydrocarbons can be aliphatic or aromatic; aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes.
- The combustion of hydrocarbons is a primary source of energy for our society.

? Exercise 22.2.2

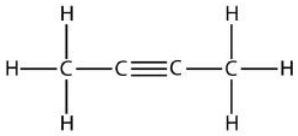
1. Define *hydrocarbon*. What are the two general types of hydrocarbons?
2. What are the three different types of aliphatic hydrocarbons? How are they defined?
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

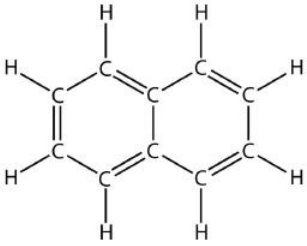
a. 

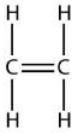
b. 

c. 

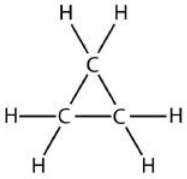
4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

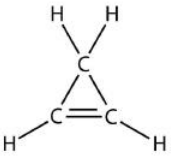
a. 

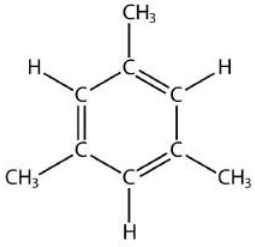
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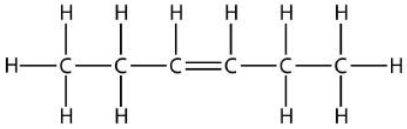
5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

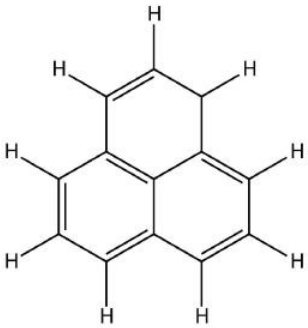
a. 

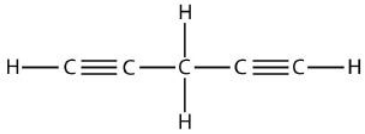
b. 

c. 

6. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

b. 

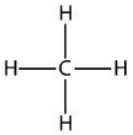
c. 

7. Name and draw the structural formulas for the four smallest alkanes.
8. Name and draw the structural formulas for the four smallest alkenes.
9. What does the term *aromatic* imply about an organic molecule?
10. What does the term *normal* imply when used for alkanes?
11. Explain why the name *1-propene* is incorrect. What is the proper name for this molecule?
12. Explain why the name *3-butene* is incorrect. What is the proper name for this molecule?
13. Name and draw the structural formula of each isomer of pentene.
14. Name and draw the structural formula of each isomer of hexyne.
15. Write a chemical equation for the reaction between methane and bromine.
16. Write a chemical equation for the reaction between ethane and chlorine.
17. Draw the structure of the product of the reaction of bromine with propene.
18. Draw the structure of the product of the reaction of chlorine with 2-butene.
19. Draw the structure of the product of the reaction of hydrogen with 1-butene.
20. Draw the structure of the product of the reaction of hydrogen with 1-butene.
21. Write the balanced chemical equation for the combustion of heptane.
22. Write the balanced chemical equation for the combustion of nonane.

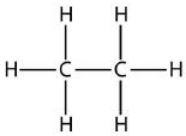
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Answers

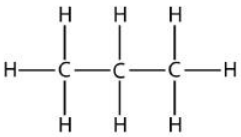
1. an organic compound composed of only carbon and hydrogen; aliphatic hydrocarbons and aromatic hydrocarbons
2.
3. a. aliphatic; alkane
   b. aromatic
   c. aliphatic; alkene
4.
5. a. aliphatic; alkane
   b. aliphatic; alkene
   c. aromatic
6.



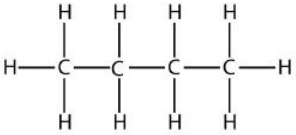
Methane



Ethane

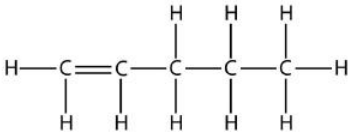


Propane

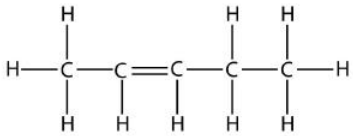


Butane

7.
8.
9. Aromatic means that the molecule has a benzene ring.
10.
11. The 1 is not necessary. The name of the compound is simply *propene*.
12.



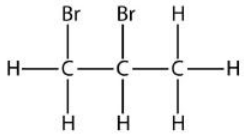
1-Pentene



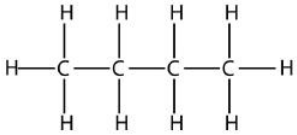
2-Pentene

13.
14.
15. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$

16.

17. 

18.

19. 

20.

21. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

This page titled 22.2: Hydrocarbons- Compounds Containing Only Carbon and Hydrocarbon is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by Anonymous via source content that was edited to the style and standards of the LibreTexts platform.

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22.3: Polymers

Learning Objective

- To understand polymer synthesis.
- To understand the differences between synthetic and biological polymers.

Most of the solids discussed so far have been molecules or ions with low molecular masses, ranging from tens to hundreds of atomic mass units. Many of the molecular materials in consumer goods today, however, have very high molecular masses, ranging from thousands to millions of atomic mass units, and are formed from a carefully controlled series of reactions that produce giant molecules called polymersA giant molecule that consists of many basic structural units (monomers) connected in a chain or network by covalent bonds. (from the Greek *poly* and *meros*, meaning “many parts”). Polymers are used in corrective eye lenses, plastic containers, clothing and textiles, and medical implant devices, among many other uses. They consist of basic structural units called monomersThe basic structural unit of a polymer., which are repeated many times in each molecule. As shown schematically in Figure 8.8.1 , polymerizationA process by which monomers are connected into chains or networks by covalent bonds. is the process by which monomers are connected into chains or networks by covalent bonds. Polymers can form via a *condensation reaction*, in which two monomer molecules are joined by a new covalent bond and a small molecule such as water is eliminated, or by an *addition reaction*, a variant of a condensation reaction in which the components of a species AB are added to adjacent atoms of a multiple bond. Many people confuse the terms *plastics* and *polymers*. PlasticThe property of a material that allows it to be molded into almost any shape. is the property of a material that allows it to be molded into almost any shape. Although many plastics are polymers, many polymers are not plastics. In this section, we introduce the reactions that produce naturally occurring and synthetic polymers.

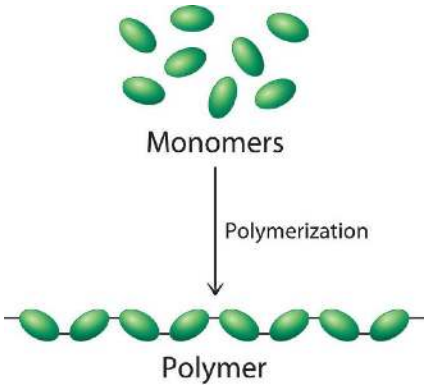


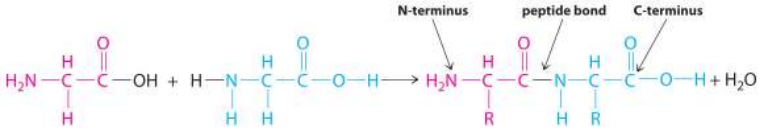
Figure 8.8.1 Polymer formation during a polymerization reaction, *a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.*

Note the Pattern

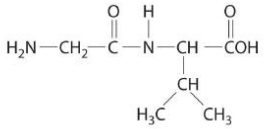
Polymers are formed via condensation or addition reactions.

Naturally Occurring Polymers: Peptides and Proteins

Polymers that occur naturally are crucial components of all organisms and form the fabric of our lives. Hair, silk, skin, feathers, muscle, and connective tissue are all primarily composed of proteins, the most familiar kind of naturally occurring, or biological, polymer. The monomers of many biological polymers are the amino acids each called an *amino acid residue*. The residues are linked together by amide bonds, also called peptide bonds, via a condensation reaction where H_2O is eliminated:



In the above equation, R represents an alkyl or aryl group, or hydrogen, depending on the amino acid. We write the structural formula of the product with the free amino group on the left (the *N-terminus*) and the free carboxylate group on the right (the *C-terminus*). For example, the structural formula for the product formed from the amino acids glycine and valine (glycyl-valine) is as follows:



Glycyl-valine

The most important difference between synthetic and naturally occurring polymers is that the former usually contain very few different monomers, whereas biological polymers can have as many as 20 different kinds of amino acid residues arranged in many different orders. Chains with less than about 50 amino acid residues are called peptidesBiological polymers with less than about 50 amino acid residues., whereas those with more than about 50 amino acid residues are called proteinsBiological polymers with more than 50 amino acid residues linked together by amide bonds.. Many proteins are enzymesCatalysts that occur naturally in living organisms and that catalyze biological reactions., which are catalysts that increase the rate of a biological reaction.

Note the Pattern

Synthetic polymers usually contain only a few different monomers, whereas biological polymers can have many kinds of monomers, such as amino acids arranged in different orders.

Many small peptides have potent physiological activities. The *endorphins*, for example, are powerful, naturally occurring painkillers found in the brain. Other important peptides are the hormones vasopressin and oxytocin. Although their structures and amino acid sequences are similar, vasopressin is a blood pressure regulator, whereas oxytocin induces labor in pregnant women and milk production in nursing mothers. Oxytocin was the first biologically active peptide to be prepared in the laboratory by Vincent du Vigneaud (1901–1978), who was awarded the Nobel Prize in Chemistry in 1955.

Synthetic Polymers

Many of the synthetic polymers we use, such as plastics and rubbers, have commercial advantages over naturally occurring polymers because they can be produced inexpensively. Moreover, many synthetic polymers are actually more desirable than their natural counterparts because scientists can select monomer units to tailor the physical properties of the resulting polymer for particular purposes. For example, in many applications, wood has been replaced by plastics that are more durable, lighter, and easier to shape and maintain. Polymers are also increasingly used in engineering applications where weight reduction and corrosion resistance are required. Steel rods used to support concrete structures, for example, are often coated with a polymeric material when the structures are near ocean environments where steel is vulnerable to corrosion (For more information on corrosion, see Section 17.6.) In fact, the use of polymers in engineering applications is a very active area of research.

Probably the best-known example of a synthetic polymer is *nylon* (Figure 8.8.2). Its monomers are linked by amide bonds (which are called peptide bonds in biological polymers), so its physical properties are similar to those of some proteins because of their common structural unit—the amide group. Nylon is easily drawn into silky fibersA particle of a synthetic polymer that is more than 100 times longer than it is wide. that are more than a hundred times longer than they are wide and can be woven into fabrics. Nylon fibers are so light and strong that during World War II, all available nylon was commandeered for use in parachutes, ropes, and other military items. With polymer chains that are fully extended and run parallel to the fiber axis, nylon fibers resist stretching, just like naturally occurring silk fibers, although the structures of nylon and silk are otherwise different. Replacing the flexible $–CH_2–$ units in nylon by aromatic rings produces a stiffer and stronger polymer, such as the very strong polymer known as Kevlar. Kevlar fibers are so strong and rigid that they are used in lightweight army helmets, bulletproof vests, and even sailboat and canoe hulls, all of which contain multiple layers of Kevlar fabric.

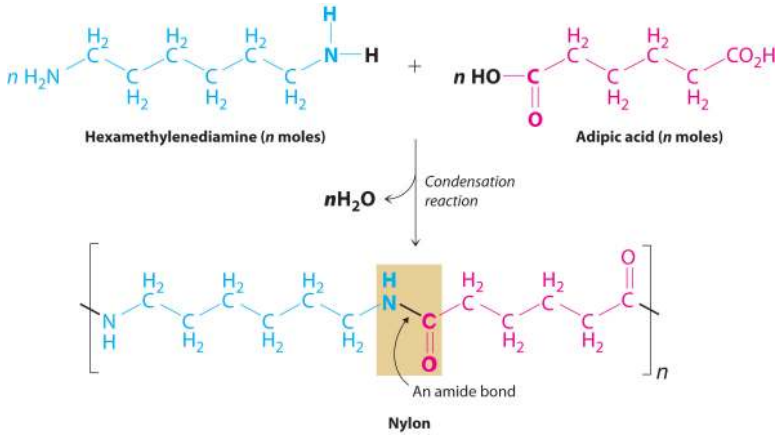


Figure 8.8.2 The Synthesis of Nylon *Nylon is a synthetic condensation polymer created by the reaction of a dicarboxylic acid and a diamine to form amide bonds and water.*



esis of Nylon: *A video showing the synthesis of nylon 6,10 by Mabakken*

Not all synthetic polymers are linked by amide bonds—for example, *polyesters* contain monomers that are linked by ester bonds. Polyesters are sold under trade names such as Dacron, Kodel, and Fortrel, which are used in clothing, and Mylar, which is used in magnetic tape, helium-filled balloons, and high-tech sails for sailboats. Although the fibers are flexible, properly prepared Mylar films are almost as strong as steel.

Polymers based on skeletons with only carbon are all synthetic. Most of these are formed from ethylene (CH_2=CH_2), a two-carbon building block, and its derivatives. The relative lengths of the chains and any branches control the properties of polyethylene. For

example, higher numbers of branches produce a softer, more flexible, lower-melting-point polymer called low-density polyethylene (LDPE), whereas high-density polyethylene (HDPE) contains few branches. Substances such as glass that melt at relatively low temperatures can also be formed into fibers, producing *fiberglass*.



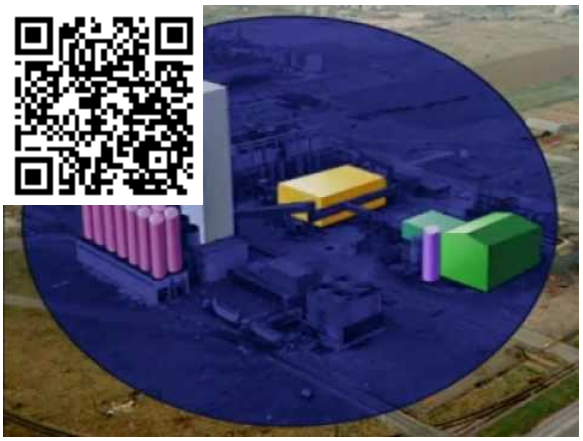


Figure 8.8.4 Commercial Polyethene production: *A video discussing the commercial production of polyethene from the Royal Society of Chemistry*

Because most synthetic fibers are neither soluble nor low melting, multistep processes are required to manufacture them and form them into objects. Graphite fibers are formed by heating a precursor polymer at high temperatures to decompose it, a process called pyrolysisA high-temperature decomposition reaction that can be used to form fibers of synthetic polymers.. The usual precursor for graphite is polyacrylonitrile, better known by its trade name—Orlon. A similar approach is used to prepare fibers of silicon carbide using an organosilicon precursor such as polydimethylsilane $\{[–(CH_3)_2Si–]_n\}$. A new type of fiber consisting of carbon nanotubes, hollow cylinders of carbon just one atom thick, is lightweight, strong, and impact resistant. Its performance has been compared to that of Kevlar, and it is being considered for use in body armor, flexible solar panels, and bombproof trash bins, among other uses.

Because there are no good polymer precursors for elemental boron or boron nitride, these fibers have to be prepared by time-consuming and costly indirect methods. Even though boron fibers are about eight times stronger than metallic aluminum and 10% lighter, they are significantly more expensive. Consequently, unless an application requires boron's greater resistance to oxidation, these fibers cannot compete with less costly graphite fibers.

Example 8.8.1

Polyethylene is used in a wide variety of products, including beach balls and the hard plastic bottles used to store solutions in a chemistry laboratory. Which of these products is formed from the more highly branched polyethylene?

Given: type of polymer

Asked for: application

Strategy:

Determine whether the polymer is LDPE, which is used in applications that require flexibility, or HDPE, which is used for its strength and rigidity.

Solution:

A highly branched polymer is less dense and less rigid than a relatively unbranched polymer. Thus hard, strong polyethylene objects such as bottles are made of HDPE with relatively few branches. In contrast, a beach ball must be flexible so it can be inflated. It is therefore made of highly branched LDPE.

Exercise

Which products are manufactured from LDPE and which from HPDE?

1. lawn chair frames
2. rope
3. disposable syringes
4. automobile protective covers

Answer

1. HDPE
2. LDPE
3. HDPE
4. LDPE

Summary

Polymers are giant molecules that consist of long chains of units called **monomers** connected by covalent bonds. **Polymerization** is the process of linking monomers together to form a polymer. **Plastic** is the property of a material that allows it to be molded. Biological polymers formed from amino acid residues are called **peptides** or **proteins**, depending on their size. **Enzymes** are proteins that catalyze a biological reaction. A particle that is more than a hundred times longer than it is wide is a **fiber**, which can be formed by a high-temperature decomposition reaction called **pyrolysis**.

Key Takeaway

- Polymers are giant molecules formed from addition or condensation reactions and can be classified as either biological or synthetic polymers.

Conceptual Problems

1. How are amino acids and proteins related to monomers and polymers? Draw the general structure of an amide bond linking two amino acid residues.
2. Although proteins and synthetic polymers (such as nylon) both contain amide bonds, different terms are used to describe the two types of polymer. Compare and contrast the terminology used for the
    1. smallest repeating unit.
    2. covalent bond connecting the units.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Nylon synthesis from MA Bakken @ YouTube

Polyethylene production from Royal Society of Chemistry @ YouTube

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22.4: Alkanes- Saturated Hydrocarbons

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *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.

> 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 22.4.1.

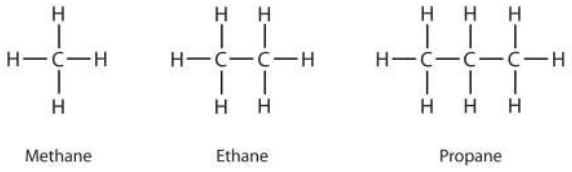


Figure 22.4.1: The Three Simplest Alkanes

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 22.4.2).

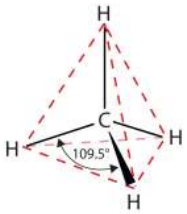


Figure 22.4.2: The Tetrahedral Methane Molecule

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 22.4.1.

Table 22.4.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure 22.4.3. 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.

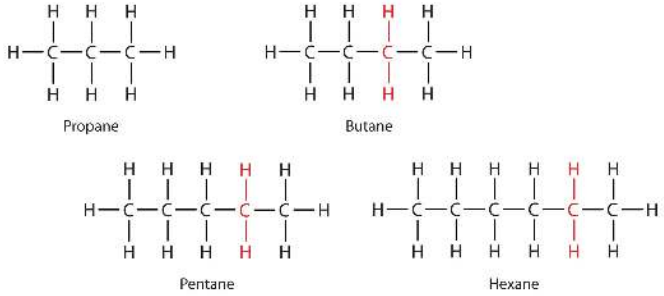


Figure 22.4.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2\times 8)+2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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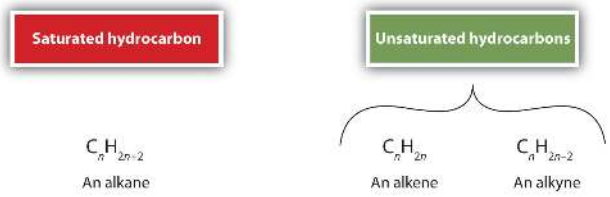
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22.5: Alkenes and Alkynes

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

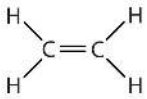


Some representative alkenes—their names, structures, and physical properties—are given in Table 22.5.1.

Table 22.5.1: 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 22.5.1. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table 22.5.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 22.5.1). 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.

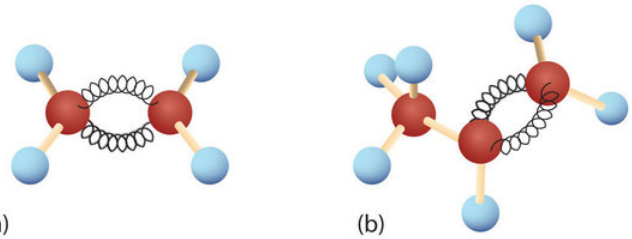
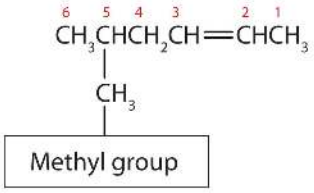


Figure 22.5.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

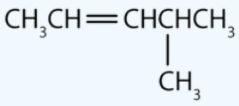
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

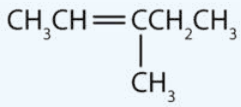
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



Example 22.5.1

Name each compound.

a. 

b. 

Solution

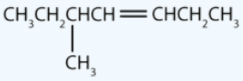
a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.

b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 22.5.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

Answer

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 22.5.2

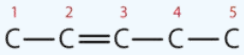
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

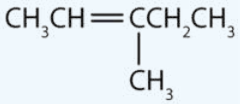
Solution

a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

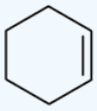


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



Exercise 22.5.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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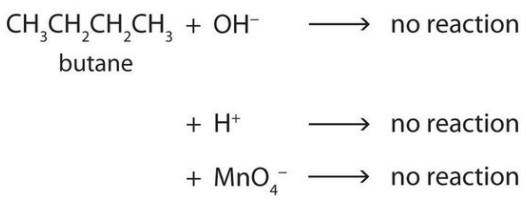
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22.6: Hydrocarbon Reactions

Learning Objectives

- To identify the main chemical properties of alkanes.

Alkane molecules are nonpolar and therefore generally do not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents. Consider butane as an example:



Butane plus O H superscript negative sign yields no reaction. There is also no reaction of butane with H superscript positive sign and Mn O subscript 4 superscript negative sign.

Neither positive ions nor negative ions are attracted to a nonpolar molecule. In fact, the alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning "little affinity."

Two important reactions that the alkanes do undergo are combustion and halogenation. Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the reaction is as follows:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + \text{heat}$$

If the reactants are adequately mixed and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and heat—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, however, other products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2\,CH_4 + 3\,O_2 \rightarrow 2\,CO + 4\,H_2O$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Alkanes also react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

With more chlorine, a mixture of products is obtained: CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

Key Takeaway

- Alkanes react with oxygen (combustion) and with halogens (halogenation).

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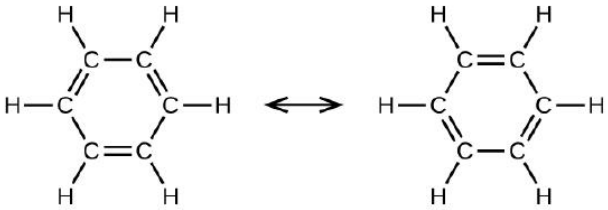
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22.7: Aromatic Hydrocarbons

Textbook, Hydrocarbons

Textbook, Hydrocarbons

Benzene, C_6H_6, is the simplest member of a large family of hydrocarbons, called aromatic hydrocarbons. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C_6H_6, are:



Benzene is shown as a hexagonal ring. There are three double bonds in total. The left structure shows double bonds occupying three sides of the hexagon. A double sided arrow points to the right structure which has three double bonds which occupy the three previously unoccupied sides on the left.

Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as hexagonal rings of sp^2-hybridized carbon atoms with the unhybridized *p* orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the sp^2 hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of σ bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized *p* orbitals to yield the π bonds. Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a $\mathrm{C=C}$ double bond. To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in Figure 22.7.10.

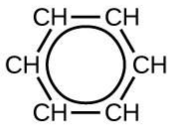
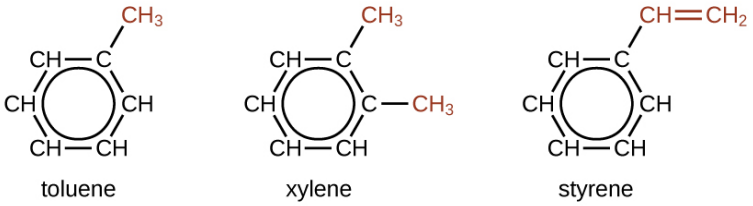


Figure 22.7.10: This condensed formula shows the unique bonding structure of benzene.
A six carbon hexagonal ring structural formula is shown. Each C has an H atom beside it. A circle is at the center of the ring.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:

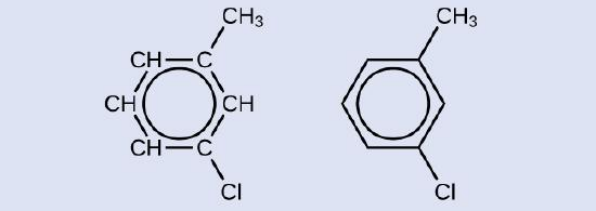


Toluene has one of the H replaced by C H subscript 3 molecule. Xylene has 2 of the H atoms replaced by two C H subscript 3 molecules respectively. Styrene has one of the H atom replaced C H double bond C H subscript 2.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

Structure of Aromatic Hydrocarbons

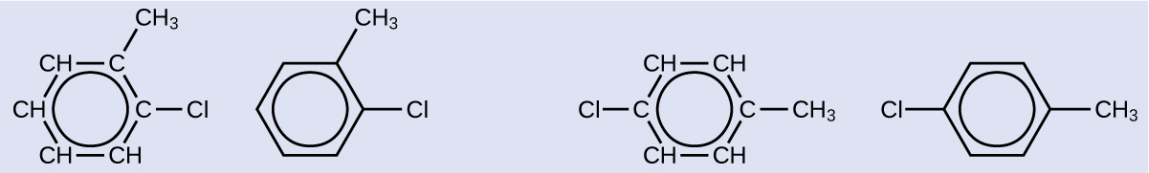
One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



A hexagonal structure of benzene is shown with one of the H replaced by a chlorine atom and another H replaced by C H subscript 3. These two substitutions are apart by 1 carbon atom. Two structures are shown, one shows all the C and H in the ring written out, while the other omits it.

Solution

Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:

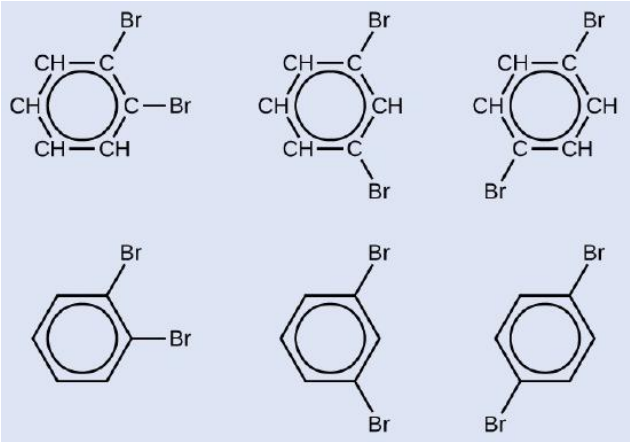


A hexagonal structure of benzene is shown with one of the H replaced by a chlorine atom and another H replaced by C H subscript 3. There are two of these isomers. The first isomer has these two substitutions adjacent to one another while the other are apart by 2 carbons. Two structures are shown for each isomer, one shows all the C and H in the ring written out, while the other omits it.

Exercise 22.7.7

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Answer



A hexagonal structure of benzene is shown with two of the H replaced by two bromine atoms. Three of these isomers are shown. The first isomer has these two substitutions adjacent to one another, the next isomer has these two bromines 1 carbon apart and the final isomer has two bromines that are two carbons apart. Two structures are shown for each isomer, one shows all the C and H in the ring written out, while the other omits it.

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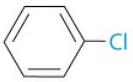
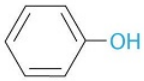
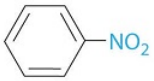
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22.8: Functional Groups

Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

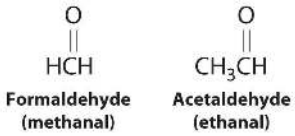
You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure 22.8.1 summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX[a]		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH[b]		phenol	-ol
Ethers	ROR′	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO	$CH_3\overset{O}{\overset{\|}{C}}H$	acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	RR′C=O	$CH_3\overset{O}{\overset{\|}{C}}CH_3$	acetone (2-propanone)	-one
Carboxylic acids	RCO_2H	$CH_3\overset{O}{\overset{\|}{C}}OH$	acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'	$CH_3\overset{O}{\overset{\|}{C}}OCH_3$	methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR′	$CH_3\overset{O}{\overset{\|}{C}}NHCH_3$	*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, RNHR′, RNR′R″	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

[a]R indicates an alkyl group [b]Ar indicates an aryl group Figure 22.8.1: Major Classes of Organic Compounds

The first family listed in Figure 22.8.1 is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by $C_nH_{2n−2}$; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $–CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $–NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C=O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 22.8.2). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para- compounds, the name is meta-xylene or m-xylene.

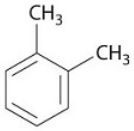
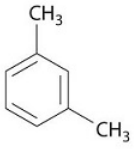
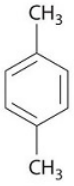
Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
ortho-	1,2		*o*-xylene (1,2-dimethylbenzene)
meta-	1,3		*m*-xylene (1,3-dimethylbenzene)
para-	1,4		*p*-xylene (1,4-dimethylbenzene)

Figure 22.8.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

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22.9: Alcohols

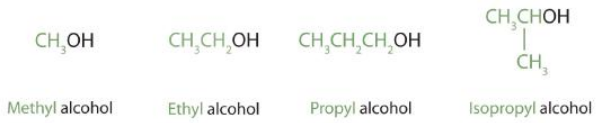
Learning Objectives

- Identify the general structure for an alcohol.
- Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
- Name alcohols with both common names and IUPAC names

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are the first two members of the homologous series of alcohols.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:



Structural formula of methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol with the methyl, ethyl propyl, and isopropyl groups highlighted in green.

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

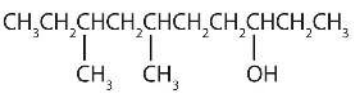
1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
2. The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the *-e* ending of the parent alkane is replaced by the suffix *-ol*. (In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
3. If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

Figure 22.9.1 shows some examples of the application of these rules.

Structures of 2 methylbutan-2-ol, 3 5-dimethylhexan-1-ol, 6 methylheptan-3-ol, 2 bromo 5 chlorocyclopentanol are shown to highlight rules 1 and 2. 1 2 ethanediol and propane 1 2 3 triol are shown to highlight rule 3
Figure 22.9.1: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

Example 22.9.1

Give the IUPAC name for each compound.

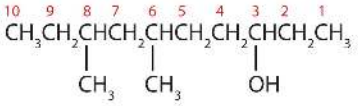
a. 

From left to right, there are ten carbon on the alkane straight chain with methyl groups emerging from carbon 3 and 5 and a hydroxyl group on carbon 8.

- $HOCH_2CH_2CH_2CH_2CH_2OH$

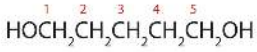
Solution

a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).



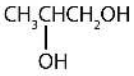
The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH_3) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

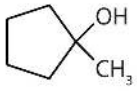
b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).



? Exercise 22.9.1

Give the IUPAC name for each compound.

a. 

- 

✔ Example 22.9.2

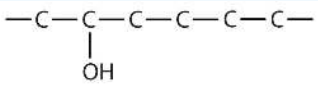
Draw the structure for each compound.

a. 2-hexanol
b. 3-methyl-2-pentanol

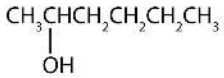
Solution

a. The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: –C–C–C–C–C–C–.

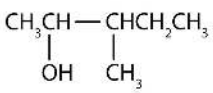
The 2 indicates that the OH group is attached to the second carbon atom.



Finally, we add enough hydrogen atoms to give each carbon atom four bonds.



- The numbers indicate that there is a methyl (CH_3) group on the third carbon atom and an OH group on the second carbon atom.



? Exercise 22.9.2

Draw the structure for each compound.

a. 3-heptanol

- 2-methyl-3-hexanol

Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A primary (1°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is RCH_2OH.



- A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is R_2CHOH.



- A tertiary (3°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is R_3COH.

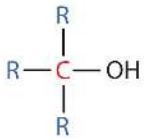
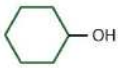


Table 22.9.1 names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:



Table 22.9.1: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH_3OH	—	methyl alcohol	methanol
CH_3CH_2OH	primary	ethyl alcohol	ethanol
$CH_3CH_2CH_2OH$	primary	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	secondary	isopropyl alcohol	2-propanol
$CH_3CH_2CH_2CH_2OH$	primary	butyl alcohol	1-butanol
$CH_3CH_2CHOHCH_3$	secondary	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	primary	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	tertiary	*tert*-butyl alcohol	2-methyl-2-propanol
	secondary	cyclohexyl alcohol	cyclohexanol

Summary

In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol*. Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.

Learning Objectives

- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.

Alcohols can be considered derivatives of water (H_2O; also written as HOH).



Like the H–O–H bond in water, the R–O–H bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure 22.9.1).

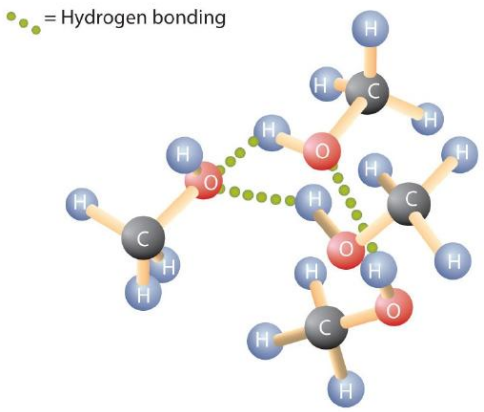


Figure 22.9.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 22.9.1 lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table 22.9.1: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point (°C)
CH_4	methane	16	–164
HOH	water	18	100
C_2H_6	ethane	30	–89
CH_3OH	methanol	32	65
C_3H_8	propane	44	–42
CH_3CH_2OH	ethanol	46	78
C_4H_{10}	butane	58	–1
$CH_3CH_2CH_2OH$	1-propanol	60	97

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules (Figure 22.9.2). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.

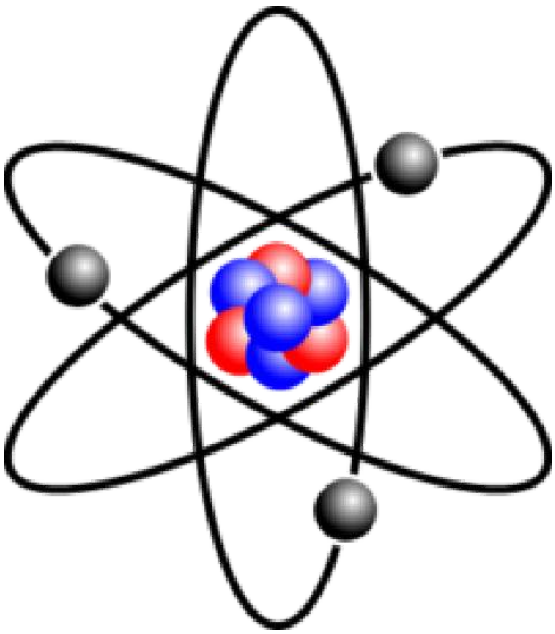


Figure 22.9.2: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

Summary

Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.

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 22.9.1, two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.

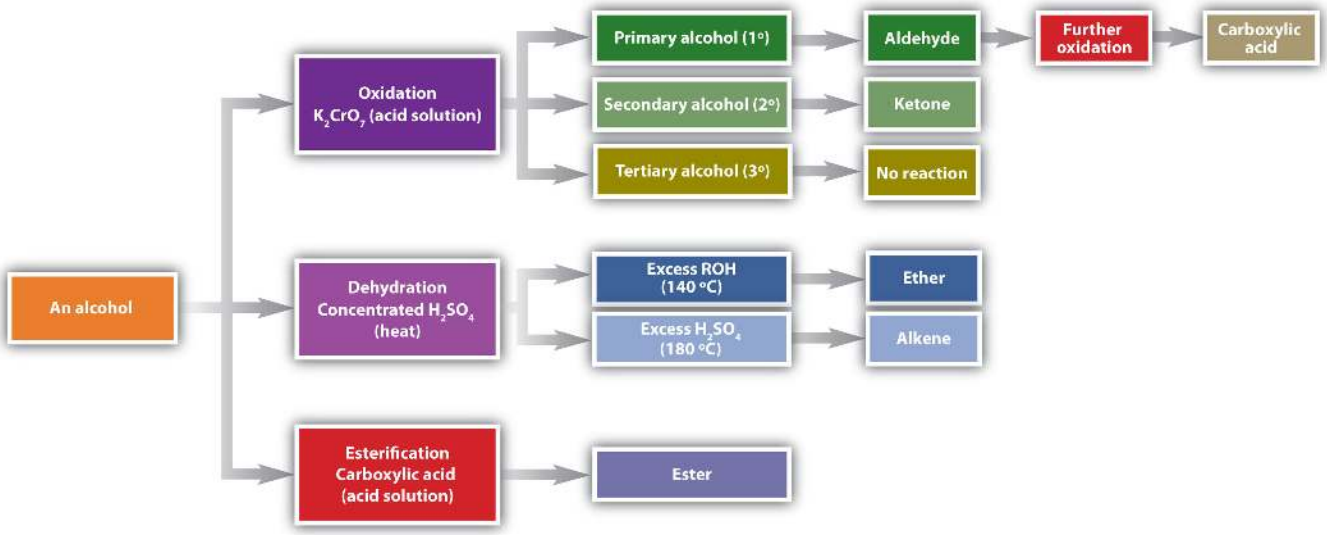
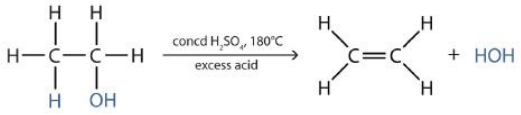


Figure 22.9.1: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.

A flow diagram of three possible reactions of an alcohol. The final products of the reactions are also shown at the end of the flow diagram.

Dehydration

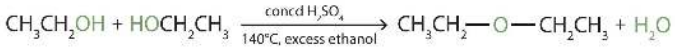
As noted in Figure 22.9.1, an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule:



Ethanol Ethylene

Structural formula of ethanol dehydrating under excess concentrated sulfuric acid at 180 degrees celsius. The products are ethylene and a side product of a water molecule.

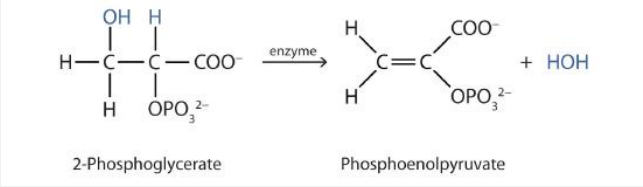
Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.



Two molecules of ethanol are dehydrated under concentrated sulfuric acid at 140 degrees celsius and excess ethanol to give a diethyl ether and a water molecule.

(Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

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

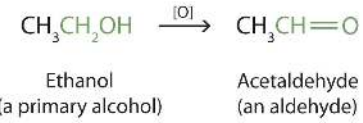


Structural formula of 2 phosphoglycerate forming phosphoenolpyruvate and a water molecule with the aid of enzymes.

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.

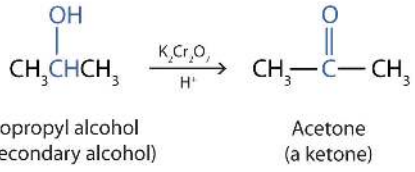
Oxidation

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:



Formula of ethanol reacting to form acetaldehyde with an O in a bracket above the right pointing arrow.

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:

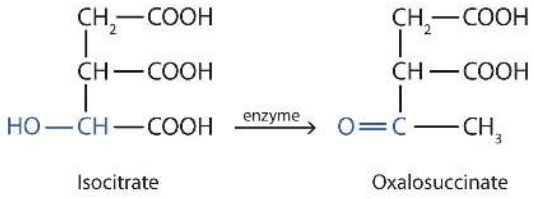


Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH_2OH) and secondary (R_2CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

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:

$$8\,H^{=} + Cr_2O_7^{2-} + 3\,CH_3CH_2OH \longrightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O$$

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

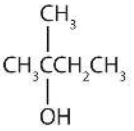
The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

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.

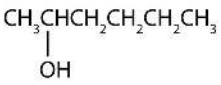
Example 22.9.1

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.

a. $CH_3CH_2CH_2CH_2CH_2OH$

b. 

From left to right, there are four carbons on the alkane straight chain with a methyl and hydroxyl group on carbon 2.

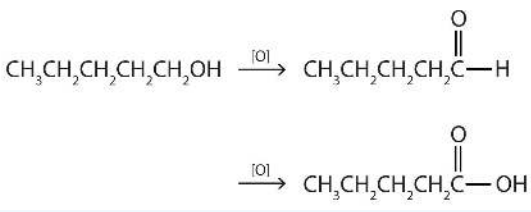
c. 

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group on carbon 2.

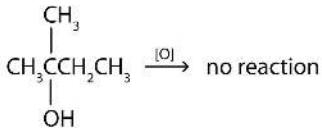
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

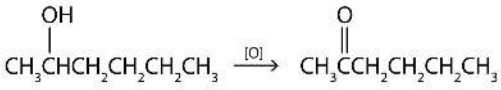
a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



b. 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.



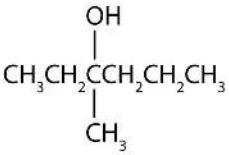
c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.



? Exercise 22.9.1

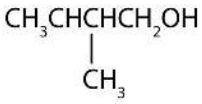
Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write “no reaction” after the arrow.

a.



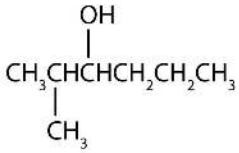
From left to right, there are six carbons on the alkane straight chain with a hydroxyl group and methyl group on carbon 3.

b.



From left to right, there are four carbons on the alkane straight chain with a methyl group on carbon 3 as well as a hydroxyl group on carbon 4.

c.



From left to right, there are six carbons on the alkane straight chain with a methyl group on carbon 2 and a hydroxyl group on carbon 3.

Summary

Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

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22.10: Aldehydes and Ketones

Learning Objectives

- Identify the general structure for an aldehyde and a ketone.
- Use common names to name aldehydes and ketones.
- Use the IUPAC system to name aldehydes and ketones.

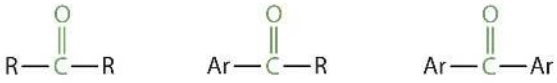
The next functional group we consider, the carbonyl group, has a carbon-to-oxygen double bond.



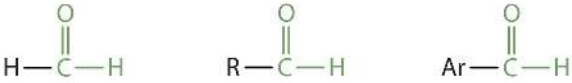
Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones.

> *The carbonyl group is ubiquitous in biological compounds. It is found in carbohydrates, fats, proteins, nucleic acids, hormones, and vitamins—organic compounds critical to living systems.*

In a ketone, two carbon groups are attached to the carbonyl carbon atom. The following general formulas, in which R represents an alkyl group and Ar stands for an aryl group, represent ketones.



In an aldehyde, at least one of the attached groups must be a hydrogen atom. The following compounds are aldehydes:



In condensed formulas, we use CHO to identify an aldehyde rather than COH, which might be confused with an alcohol. This follows the general rule that in condensed structural formulas H comes after the atom it is attached to (usually C, N, or O).



An aldehyde

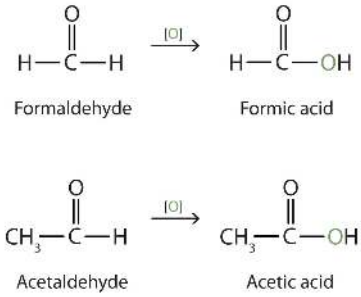


A ketone

The carbon-to-oxygen double bond is not shown but understood to be present. Because they contain the same functional group, aldehydes and ketones share many common properties, but they still differ enough to warrant their classification into two families.

Naming Aldehydes and Ketones

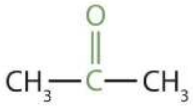
Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.



The stems for the common names of the first four aldehydes are as follows:

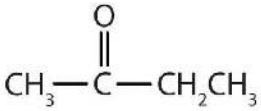
- 1 carbon atom: *form-*
- 2 carbon atoms: *acet-*
- 3 carbon atoms: *propion-*
- 4 carbon atoms: *butyr-*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.



Acetone

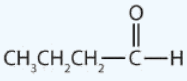
Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.

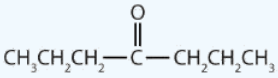


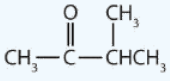
Ethyl methyl ketone

Example 22.10.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

a. 

b. 

c. 

Solution

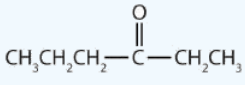
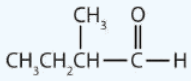
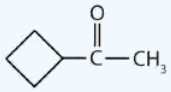
a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.

c. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

Exercise 22.10.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

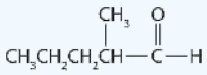
1. 
2. 
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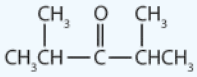
Here are some simple IUPAC rules for naming aldehydes and ketones:

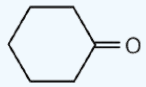
- The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
- For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
- For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
- To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
- To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

Example 22.10.2

Give the IUPAC name for each compound.

a. 

b. 

c. 

Solution

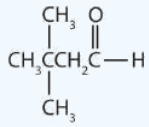
a. There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.

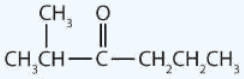
b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.

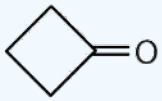
c. There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

Exercise

Give the IUPAC name for each compound.

a. 

b. 

c. 

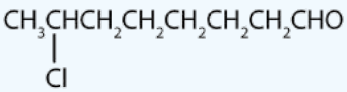
Example 22.10.3

Draw the structure for each compound.

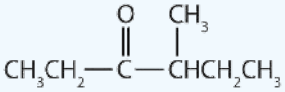
a. 7-chlorooctanal
b. 4-methyl–3-hexanone

Solution

a. The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.



b. The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH_3) group at C4:



Exercise 22.10.3

Draw the structure for each compound.

a. 5-bromo-3-iodoheptanal
b. 5-bromo-4-ethyl-2-heptanone

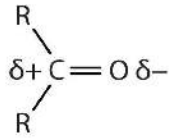
Summary

The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

Learning Objectives

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Name the typical reactions take place with aldehydes and ketones.
- Describe some of the uses of common aldehydes and ketones.

The carbon-to-oxygen double bond is quite polar, more polar than a carbon-to-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge:



In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 22.10.1 shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

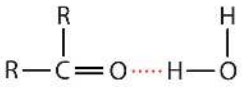
Table 22.10.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass	Type of Intermolecular Forces	Boiling Point (°C)
$CH_3CH_2CH_2CH_3$	alkane	58	dispersion only	–1
$CH_3OCH_2CH_3$	ether	60	weak dipole	6
CH_3CH_2CHO	aldehyde	58	strong dipole	49
$CH_3CH_2CH_2OH$	alcohol	60	hydrogen bonding	97

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

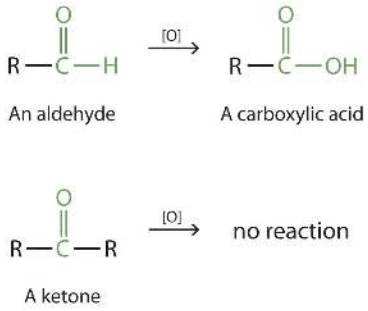
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.



The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

Oxidation of Aldehydes and Ketones

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.



The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen (O_2) in air to carboxylic acids.

$$2\,RCHO + O_2 \longrightarrow 2\,RCOOH$$

The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. Tollens' reagent, for example, is an alkaline solution of silver (Ag^+) ion complexed with ammonia (NH_3), which keeps the Ag^+ ion in solution.

$$H_3N{-}Ag^+{-}NH_3$$

When Tollens' reagent oxidizes an aldehyde, the Ag^+ ion is reduced to free silver (Ag).

$$\underbrace{RCHO\,(aq)}_{\text{an aldehyde}} + 2\,Ag(NH_3)_2{}^+\,(aq) \longrightarrow RCOO^- + \underbrace{2\,Ag\,(s)}_{\text{free silver}} + 4\,NH_3\,(aq) + 2\,H_2O$$

Deposited on a clean glass surface, the silver produces a mirror (Figure 22.10.1). Ordinary ketones do not react with Tollens' reagent.



Figure 22.10.1: Aldehyde Reactions. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. Source: Photo courtesy of Krebs Glas Lauscha, commons.wikimedia.org/wiki/File:Silvering.jpg.

A person wearing gloves is holding a bunch of ornaments that she has just lifted from a basin containing a solution.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

Some Common Carbonyl Compounds

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins,

rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms.

> *The odor of green leaves is due in part to a carbonyl compound, cis-3-hexenal, which with related compounds is used to impart a "green" herbal odor to shampoos and other products.*

Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure 22.10.2).

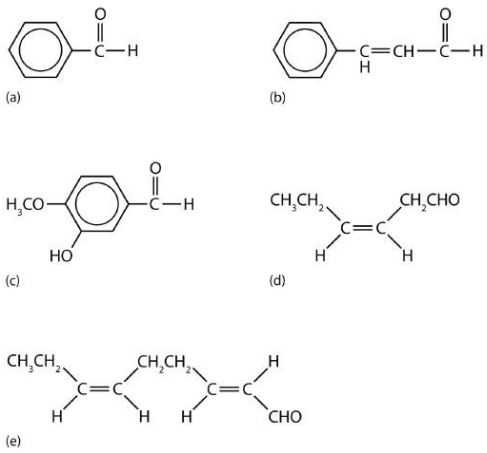


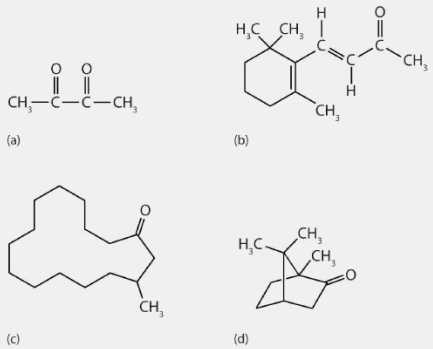
Figure 22.10.2 Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

Acetone is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail polish remover.

To Your Health: Acetone in Blood, Urine, and Breath

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.



Some ketones have interesting properties: (a) Butter flavoring comes from 2,3-butanedione; (b) β-ionone is responsible for the odor of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents.

Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone, a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone, the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

Summary

The polar carbon-to-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols that engage in intermolecular hydrogen bonding. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.

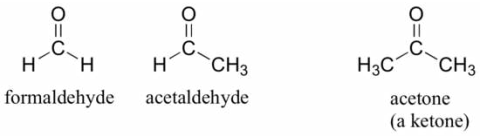
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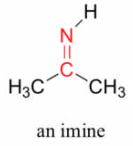
22.11: Carboxylic Acids and Esters

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.

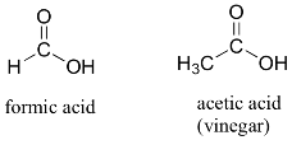


Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.

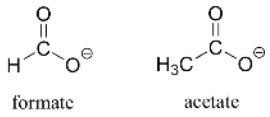


Carboxylic acids and acid derivatives

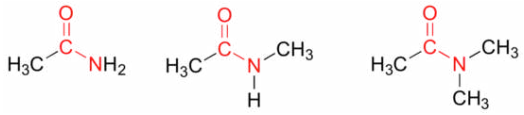
If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives'**, a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.



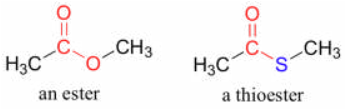
As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in the acid-base chapter!).



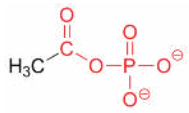
In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons, or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.

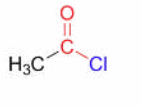


In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.

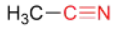


In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.

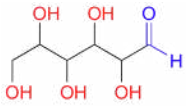

an acyl phosphate

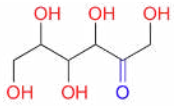

an acid chloride

Finally, in a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.

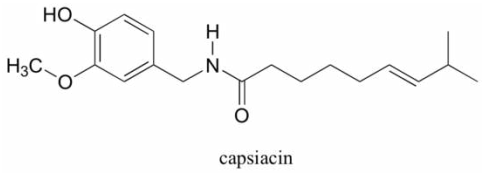

a nitrile

A single compound often contains several functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').

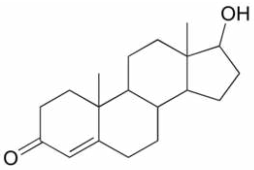

glucose

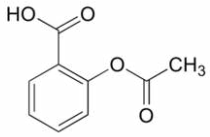

fructose

Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.


capsiacin

The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.


testosterone


acetylsalicylic acid
(aspirin)

While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table on the inside back cover provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

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22.12: Ethers

Learning Objectives

- Describe the structural difference between an alcohol and an ether that affects physical characteristics and reactivity of each.
- Name simple ethers.
- Describe the structure and uses of some ethers.

With the general formula ROR′, an ether may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups. It may also be considered a derivative of an alcohol (ROH) in which the hydrogen atom of the OH group is been replaced by a second alkyl or aryl group:

$$\mathrm{HOH} \xrightarrow[\text{H atoms}]{\text{replace both}} \mathrm{ROR'} \xleftarrow[\text{of OH group}]{\text{replace H atom}} \mathrm{ROH}$$

Simple ethers have simple common names, formed from the names of the groups attached to oxygen atom, followed by the generic name *ether*. For example, CH_3–O–$CH_2CH_2CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di-*, as in dimethyl ether (CH_3–O–CH_3) and diethyl ether CH_3CH_2–O–CH_2CH_3.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table 22.12.1).

Table 22.12.1: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

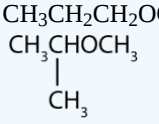
Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

Example 22.12.1

What is the common name for each ether?

a. $CH_3CH_2CH_2OCH_2CH_2CH_3$

b. 

Solution

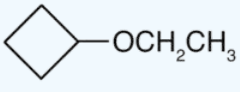
a. The carbon groups on either side of the oxygen atom are propyl ($CH_3CH_2CH_2$) groups, so the compound is dipropyl ether.

b. The three-carbon group is attached by the middle carbon atom, so it is an isopropyl group. The one-carbon group is a methyl group. The compound is isopropyl methyl ether.

? Exercise 22.12.1

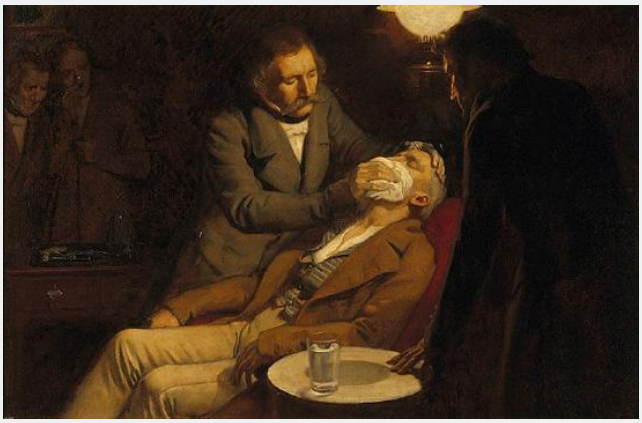
What is the common name for each ether?

a. $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$

b. 

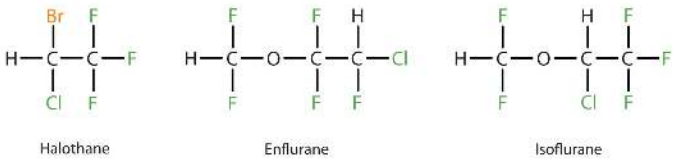
To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.



William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.

Summary

To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*. Ether molecules have no OH group and thus no intermolecular hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

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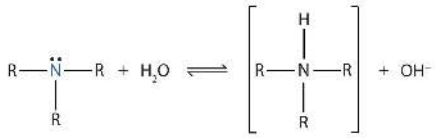
22.13: Amines

15.11: Amines - Structures and Names
15.12: Physical Properties of Amines

Learning Objectives

- Name the typical reactions that take place with amines.
- Describe heterocyclic amines.

Recall that ammonia (NH_3) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. Amines also have a lone electron pair on their nitrogen atoms and can accept a proton from water to form substituted ammonium (NH_4^+) ions and hydroxide (OH^-) ions:



As a specific example, methylamine reacts with water to form the methylammonium ion and the OH^- ion.

$$\underset{\text{Methylamine}}{CH_3NH_2(aq)} + H_2O \rightleftharpoons \underset{\text{Methylammonium ion}}{CH_3NH_3^+(aq)} + OH^-(aq)$$

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.

$$\underset{\text{Octylamine (insoluble)}}{CH_3(CH_2)_6NH_2(l)} + HNO_3(aq) \longrightarrow \underset{\text{Octylammonium nitrate (soluble)}}{CH_3(CH_2)_6NH_3{}^+NO_3^-(aq)}$$

Amine salts are named like other salts: the name of the cation is followed by the name of the anion.

Example 22.13.1

What are the formulas of the acid and base that react to form $[CH_3NH_2CH_2CH_3]^+CH_3COO^-$?

Solution

The cation has two groups—methyl and ethyl—attached to the nitrogen atom. It comes from ethylmethylamine ($CH_3NHCH_2CH_3$). The anion is the acetate ion. It comes from acetic acid (CH_3COOH).

Exercise 22.13.1

What are the formulas of the acid and base that react to form $(CH_3CH_2CH_2)_3NH^+I^-$?

To Your Health: Amine Salts as Drugs

Salts of aniline are properly named as *anilinium* compounds, but an older system, still in use for naming drugs, identifies the salt of aniline and hydrochloric acid as “aniline hydrochloride.” These compounds are ionic—they are salts—and the properties of the compounds (solubility, for example) are those characteristic of salts. Many drugs that are amines are converted to hydrochloride salts to increase their solubility in aqueous solution.

Heterocyclic Amines

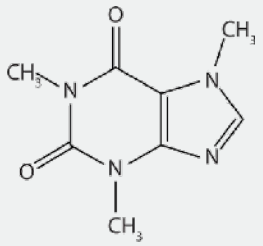
Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning “other”), nitrogen, oxygen,

sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means "like alkalis." Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

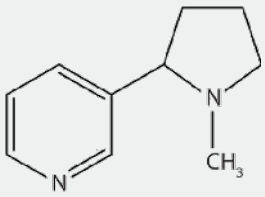
To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



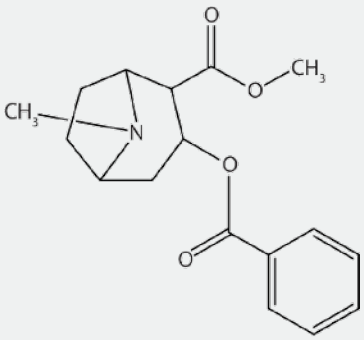
Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.



Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.

$$\underbrace{C_{17}H_{21}O_4N}_{\text{cocaine (freebase)}} + HCl \longrightarrow \text{munder}$$

Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

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CHAPTER OVERVIEW

23: Transition Metals and Coordination Compounds

Topic hierarchy

23.1: The Colors of Rubies and Emeralds
23.2: Properties of Transition Metals
23.3: Coordination Compounds
23.4: Structure and Isomerization
23.5: Bonding in Coordinate Compounds
23.6: Applications of Coordination Compounds

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23.1: The Colors of Rubies and Emeralds

Why is a ruby red? The mineral **corundum** is a crystalline form of alumina: Al_2O_3. A pure crystal of corundum is colorless. However, if just 1% of the Al^{3+} ions are replaced with Cr^{3+} ions, the mineral becomes deep red in color and is known as **ruby** (Al_2O_3:Cr^{3+}). Why does replacing Al^{3+} with Cr^{3+}in the corundum structure produce a red color?

Ruby is an *allochromatic* mineral, which means its color arises from trace impurities. The color of an *idiochromatic* mineral arises from the essential components of the mineral. In some minerals the color arises from defects in the crystal structure. Such defects are called *color centers*.

The mineral **beryl** is a crystalline beryllium aluminosilicate with the chemical formula $Be_3Al_2Si_6O_{18}$. A pure crystal of beryl is colorless. However, if just 1% of the Al^{3+} ions are replaced with Cr^{3+} ions, the mineral becomes green in color and is known as **emerald** ($Be_3Al_2Si_6O_{18}$:Cr^{3+}).

Why does replacing Al^{3+} with Cr^{3+} in corundum produce a red mineral (ruby) while replacing Al^{3+} with Cr^{3+} in beryl produces a green mineral (emerald)?

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



A piece of ruby and emerald is shown with a glassy crystalline exterior. Ruby is deep red in color and emerald is deep green.

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.

Contributors and Attributions

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23.2: Properties of Transition Metals

Learning Objectives

- Outline the general approach for the isolation of transition metals from natural sources
- Describe typical physical and chemical properties of the transition metals
- Identify simple compound classes for transition metals and describe their chemical properties

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 23.2.2, 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.

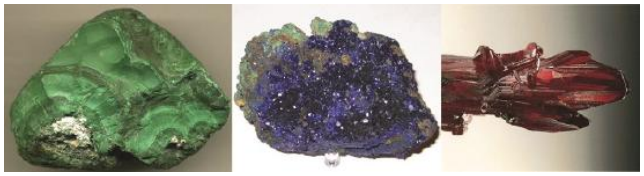


Figure 23.2.1: Transition metals often form vibrantly colored complexes. The minerals malachite (green), azurite (blue), and proustite (red) are some examples. (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace)

The first crystal is a jade green mineral chunk. The second is a crystalline chunk which is primarily bright royal blue. The third shows long red crystals.

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.

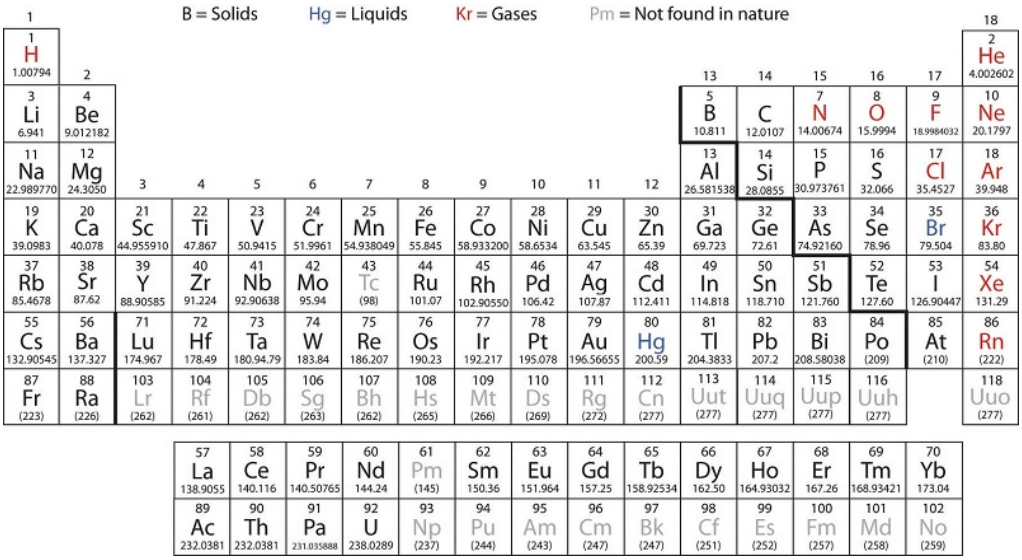


Figure 23.2.2: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

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.

Example 23.2.1: 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. $Pb^{2+}[Xe]6s^25d^{10}4f^{14}$; 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 23.2.1

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+}.

Uses of Lanthanides in Devices

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.

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 23.2.3). 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.

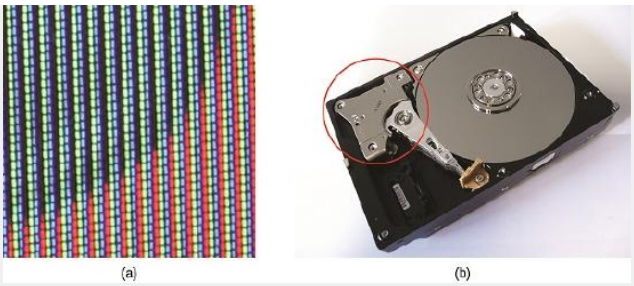


Figure 23.2.3: (a) Europium is used in display screens for televisions, computer monitors, and cell phones. (b) Neodymium magnets are commonly found in computer hard drives. (credit b: modification of work by "KUERT Datenrettung"/Flickr)

A. Closeup of a flat screen shows the many individual pixels which are red green and blue in color. B. A computer hard drive is shown with a metallic component highlighted in a red circle.

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.

Properties of the Transition Elements

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 MoO_4^{2-} and 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.

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 23.2.4. 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 23.2.4:Transition metals of the first transition series can form compounds with varying oxidation states.

Scandium has oxidation state of positive 3. Titanium has values of positive 3 and 4. Vanadium has values of positive 2 to 5. Chromium has values of positive 2,3,4, and 6. Manganese has positive 2,3,4,6, and 7. Iron has positive 2,3, and 6. Cobalt and Nickel has positive 2 and 3. Copper has positive 1,2, and 3. Zinc only has positive 2.

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+.

✔ Example 23.2.2: 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:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \quad +1.33\ V$$

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + H_2O \quad +1.51\ V$$

$$TiO_2 + 4\,H^+ + 2\,e^- \longrightarrow Ti^{2+} + 2\,H_2O \quad -0.50\ V$$

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 23.2.2

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

$Co(s) + 2\,HCl \longrightarrow H_2 + CoCl_2(aq)$; no reaction because Pt(*s*) will not be oxidized by H^+

Preparation of the Transition Elements

Ancient civilizations knew about iron, copper, silver, and gold. The time periods in human history known as the Bronze Age and Iron Age mark the advancements in which societies learned to isolate certain metals and use them to make tools and goods. Naturally occurring ores of copper, silver, and gold can contain high concentrations of these metals in elemental form (Figure 23.2.5). Iron, on the other hand, occurs on earth almost exclusively in oxidized forms, such as rust (Fe_2O_3). The earliest known iron implements were made from iron meteorites. Surviving iron artifacts dating from approximately 4000 to 2500 BC are rare, but all known examples contain specific alloys of iron and nickel that occur only in extraterrestrial objects, not on earth. It took thousands of years of technological advances before civilizations developed iron smelting, the ability to extract a pure element from its naturally occurring ores and for iron tools to become common.

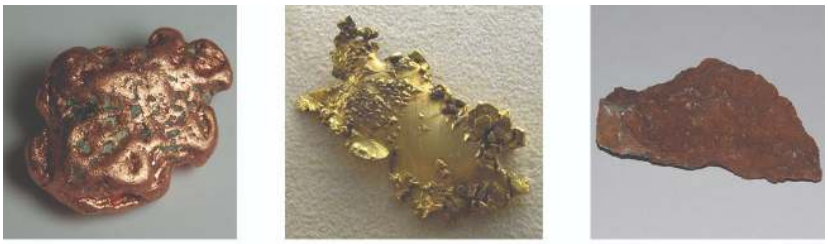


Figure 23.2.5: Transition metals occur in nature in various forms. Examples include (a) a nugget of copper, (b) a deposit of gold, and (c) an ore containing oxidized iron. (credit a: modification of work by Copper [images-of-elements.com]; credit c: modification of work by Iron ore [images-of-elements.com])

Generally, the transition elements are extracted from minerals found in a variety of ores. However, the ease of their recovery varies widely, depending on the concentration of the element in the ore, the identity of the other elements present, and the difficulty of reducing the element to the free metal.

In general, it is not difficult to reduce ions of the *d*-block elements to the free element. Carbon is a sufficiently strong reducing agent in most cases. However, like the ions of the more active main group metals, ions of the *f*-block elements must be isolated by electrolysis or by reduction with an active metal such as calcium.

We shall discuss the processes used for the isolation of iron, copper, and silver because these three processes illustrate the principal means of isolating most of the *d*-block metals. In general, each of these processes involves three principal steps: preliminary treatment, smelting, and refining.

1. Preliminary treatment. In general, there is an initial treatment of the ores to make them suitable for the extraction of the metals. This usually involves crushing or grinding the ore, concentrating the metal-bearing components, and sometimes treating these substances chemically to convert them into compounds that are easier to reduce to the metal.
2. Smelting. The next step is the extraction of the metal in the molten state, a process called smelting, which includes reduction of the metallic compound to the metal. Impurities may be removed by the addition of a compound that forms a slag—a substance with a low melting point that can be readily separated from the molten metal.
3. Refining. The final step in the recovery of a metal is refining the metal. Low boiling metals such as zinc and mercury can be refined by distillation. When fused on an inclined table, low melting metals like tin flow away from higher-melting impurities. Electrolysis is another common method for refining metals.

Isolation of Iron

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 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 23.2.6) 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.

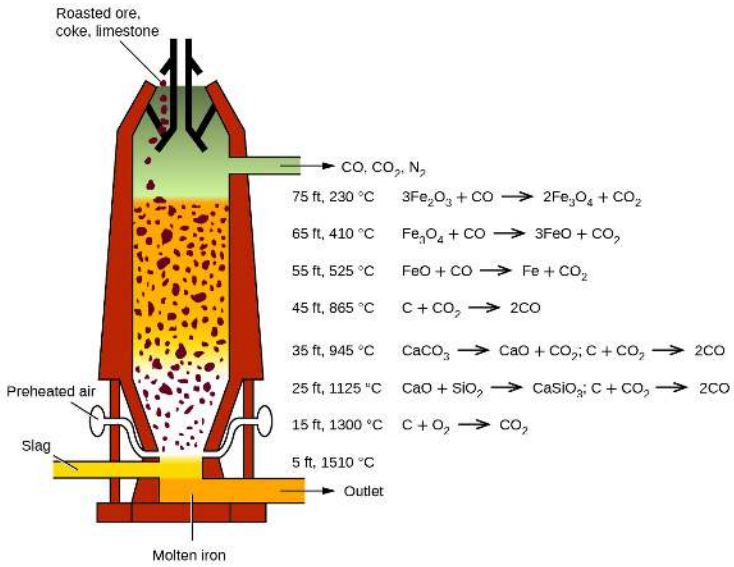


Figure 23.2.6:Within a blast furnace, different reactions occur in different temperature zones. Carbon monoxide is generated in the hotter bottom regions and rises upward to reduce the iron oxides to pure iron through a series of reactions that take place in the upper regions.

At the right side of the figure, furnace heights are labeled in order of increasing height between the outlet pipes, followed by temperatures and associated chemical reactions. Just above the pipe labeled, “Outlet,” no chemical equation at 5 f t, 1510 degrees C. At 15 f t, 1300 degrees C is the eC plus O subscript 2 right pointing arrow C O subscript 2. At 25 f t, 1125 degrees C are the two reactions, C a O plus S i O subscript 2 right pointing arrow C a S i O subscript 3 and C plus C O subscript 2 right pointing arrow 2 C O. At 35 f t, 945 degrees C, are the two reactions C a C O subscript 3 right pointing arrow C a O plus C O subscript 2, and C plus C O subscript 2 right pointing arrow 2 C O. At 45 f t, 865 degrees C is C plus C O subscript 2 right pointing arrow 2 C O. At 55 f t, 525 degrees C is the equation F e O plus C O right pointing arrow F e plus C O subscript 2. At 65 f t, 410 degrees C, is F e subscript 3 O subscript 4 plus C O right pointing arrow 3 F e O plus C O subscript 2. At 75 f t, 230 degrees C, is the equation, 3 F e subscript 2 O subscript 3 plus C O right pointing arrow 2 F e subscript 3 O subscript 4 plus C O subscript 2.

Near the bottom of a furnace are nozzles through which preheated air is blown into the furnace. As soon as the air enters, the coke in the region of the nozzles is oxidized to carbon dioxide with the liberation of a great deal of heat. The hot carbon dioxide passes upward through the overlying layer of white-hot coke, where it is reduced to carbon monoxide:

$$\mathrm{CO_2}(g) + \mathrm{C}(s) \longrightarrow 2\,\mathrm{CO}(g)$$

The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in Figure 23.2.6.

The iron oxides are reduced in the upper region of the furnace. In the middle region, limestone (calcium carbonate) decomposes, and the resulting calcium oxide combines with silica and silicates in the ore to form slag. The slag is mostly calcium silicate and contains most of the commercially unimportant components of the ore:

$$\mathrm{CaO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l)$$

Just below the middle of the furnace, the temperature is high enough to melt both the iron and the slag. They collect in layers at the bottom of the furnace; the less dense slag floats on the iron and protects it from oxidation. Several times a day, the slag and molten iron are withdrawn from the furnace. The iron is transferred to casting machines or to a steelmaking plant (Figure 23.2.7).



Figure 23.2.7:Molten iron is shown being cast as steel. (credit: Clint Budd)

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.

Isolation of Copper

The most important ores of copper contain copper sulfides (such as covellite, CuS), although copper oxides (such as tenorite, CuO) and copper hydroxycarbonates [such as malachite, $Cu_2(OH)_2CO_3$] are sometimes found. In the production of copper metal, the concentrated sulfide ore is roasted to remove part of the sulfur as sulfur dioxide. The remaining mixture, which consists of Cu_2S, FeS, FeO, and SiO_2, is mixed with limestone, which serves as a flux (a material that aids in the removal of impurities), and heated. Molten slag forms as the iron and silica are removed by Lewis acid-base reactions:

$$\mathrm{CaCO_3}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l) + \mathrm{CO_2}(g)$$

$$\mathrm{FeO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{FeSiO_3}(l)$$

In these reactions, the silicon dioxide behaves as a Lewis acid, which accepts a pair of electrons from the Lewis base (the oxide ion).

Reduction of the Cu_2S that remains after smelting is accomplished by blowing air through the molten material. The air converts part of the Cu_2S into Cu_2O. As soon as copper(I) oxide is formed, it is reduced by the remaining copper(I) sulfide to metallic copper:

$$2\,\mathrm{Cu_2S}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Cu_2O}(l) + 2\,\mathrm{SO_2}(g)$$

$$2\,\mathrm{Cu_2O}(l) + \mathrm{Cu_2S}(l) \longrightarrow 6\,\mathrm{Cu}(l) + \mathrm{SO_2}(g)$$

The copper obtained in this way is called blister copper because of its characteristic appearance, which is due to the air blisters it contains (Figure 23.2.8). This impure copper is cast into large plates, which are used as anodes in the electrolytic refining of the metal (which is described in the chapter on electrochemistry).



Figure 23.2.8: Blister copper is obtained during the conversion of copper-containing ore into pure copper. (credit: “Tortie tude”/Wikimedia Commons)

This figure shows a dull, black, lumpy mass with small, metallic flecks displayed on a clear, colorless rectangular solid base.

Isolation of Silver

Silver sometimes occurs in large nuggets (Figure 23.2.9) but more frequently in veins and related deposits. At one time, panning was an effective method of isolating both silver and gold nuggets. Due to their low reactivity, these metals, and a few others, occur in deposits as nuggets. The discovery of platinum was due to Spanish explorers in Central America mistaking platinum nuggets for silver. When the metal is not in the form of nuggets, it often useful to employ a process called hydrometallurgy to separate silver from its ores.



(a) (b)

Figure 23.2.9: Naturally occurring free silver may be found as nuggets (a) or in veins (b). (credit a: modification of work by “Teravolt”/Wikimedia Commons; credit b: modification of work by James St. John)

A. A small clump of bronze-colored metal with a very rough, irregular surface. B. A layer-like region of silver metal embedded in rock.

Hydrology involves the separation of a metal from a mixture by first converting it into soluble ions and then extracting and reducing them to precipitate the pure metal. In the presence of air, alkali metal cyanides readily form the soluble dicyanoargentate(I) ion, $[Ag(CN)_2]^-$, from silver metal or silver-containing compounds such as Ag_2S and AgCl. Representative equations are:

$$4\,Ag(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,[Ag(CN)_2]^-(aq) + 4\,OH^-(aq)$$

$$2\,Ag_2S(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,[Ag(CN)_2]^-(aq) + 2\,S(s) + 4\,OH^-(aq)$$

$$AgCl(s) + 2\,CN^-(aq) \longrightarrow [Ag(CN)_2]^-(aq) + Cl^-(aq)$$

The silver is precipitated from the cyanide solution by the addition of either zinc or iron(II) ions, which serves as the reducing agent:

$$2\,[Ag(CN)_2]^-(aq) + Zn(s) \longrightarrow 2\,Ag(s) + [Zn(CN)_4]^{2-}(aq)$$

Example 23.2.3: Refining Redox

One of the steps for refining silver involves converting silver into dicyanoargenate(I) ions:

$$4\,Ag(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,[Ag(CN)_2]^-(aq) + 4\,OH^-(aq)$$

Explain why oxygen must be present to carry out the reaction. Why does the reaction not occur as:

$$4\,Ag(s)+8\,CN^-(aq) \longrightarrow 4\,[Ag(CN)_2]^-(aq)?$$

Solution

The charges, as well as the atoms, must balance in reactions. The silver atom is being oxidized from the 0 oxidation state to the 1+ state. Whenever something loses electrons, something must also gain electrons (be reduced) to balance the equation. Oxygen is a good oxidizing agent for these reactions because it can gain electrons to go from the 0 oxidation state to the 2− state.

? Exercise 23.2.3

During the refining of iron, carbon must be present in the blast furnace. Why is carbon necessary to convert iron oxide into iron?

Answer

The carbon is converted into CO, which is the reducing agent that accepts electrons so that iron(III) can be reduced to iron(0).

Transition Metal Compounds

The bonding in the simple compounds of the transition elements ranges from ionic to covalent. In their lower oxidation states, the transition elements form ionic compounds; in their higher oxidation states, they form covalent compounds or polyatomic ions. The variation in oxidation states exhibited by the transition elements gives these compounds a metal-based, oxidation-reduction chemistry. The chemistry of several classes of compounds containing elements of the transition series follows.

Halides

Anhydrous halides of each of the transition elements can be prepared by the direct reaction of the metal with halogens. For example:

$$2\,Fe(s)+3\,Cl_2(g) \longrightarrow 2\,FeCl_3(s)$$

Heating a metal halide with additional metal can be used to form a halide of the metal with a lower oxidation state:

$$Fe(s)+2\,FeCl_3(s) \longrightarrow 3\,FeCl_2(s)$$

The stoichiometry of the metal halide that results from the reaction of the metal with a halogen is determined by the relative amounts of metal and halogen and by the strength of the halogen as an oxidizing agent. Generally, fluorine forms fluoride-containing metals in their highest oxidation states. The other halogens may not form analogous compounds.

In general, the preparation of stable water solutions of the halides of the metals of the first transition series is by the addition of a hydrohalic acid to carbonates, hydroxides, oxides, or other compounds that contain basic anions. Sample reactions are:

$$NiCO_3(s) + 2\,HF(aq) \longrightarrow NiF_2(aq) + H_2O(l) + CO_2(g)$$

$$Co(OH)_2(s) + 2\,HBr(aq) \longrightarrow CoBr_2(aq) + 2\,H_2O(l)$$

Most of the first transition series metals also dissolve in acids, forming a solution of the salt and hydrogen gas. For example:

$$Cr(s) + 2\,HCl(aq) \longrightarrow CrCl_2(aq) + H_2(g)$$

The polarity of bonds with transition metals varies based not only upon the electronegativities of the atoms involved but also upon the oxidation state of the transition metal. Remember that bond polarity is a continuous spectrum with electrons being shared evenly (covalent bonds) at one extreme and electrons being transferred completely (ionic bonds) at the other. No bond is ever 100% ionic, and the degree to which the electrons are evenly distributed determines many properties of the compound. Transition metal halides with low oxidation numbers form more ionic bonds. For example, titanium(II) chloride and titanium(III) chloride ($TiCl_2$ and $TiCl_3$) have high melting points that are characteristic of ionic compounds, but titanium(IV) chloride ($TiCl_4$) is a volatile liquid, consistent with having covalent titanium-chlorine bonds. All halides of the heavier *d*-block elements have significant covalent characteristics.

The covalent behavior of the transition metals with higher oxidation states is exemplified by the reaction of the metal tetrahalides with water. Like covalent silicon tetrachloride, both the titanium and vanadium tetrahalides react with water to give solutions containing the corresponding hydrohalic acids and the metal oxides:

$$\mathrm{SiCl_4}(l) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{SiO_2}(s) + 4\,\mathrm{HCl}(aq)$$

$$\mathrm{TiCl_4}(l) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{TiO_2}(s) + 4\,\mathrm{HCl}(aq)$$

Oxides

As with the halides, the nature of bonding in oxides of the transition elements is determined by the oxidation state of the metal. Oxides with low oxidation states tend to be more ionic, whereas those with higher oxidation states are more covalent. These variations in bonding are because the electronegativities of the elements are not fixed values. The electronegativity of an element increases with increasing oxidation state. Transition metals in low oxidation states have lower electronegativity values than oxygen; therefore, these metal oxides are ionic. Transition metals in very high oxidation states have electronegativity values close to that of oxygen, which leads to these oxides being covalent.

The oxides of the first transition series can be prepared by heating the metals in air. These oxides are Sc_2O_3, TiO_2, V_2O_5, Cr_2O_3, Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, and CuO.

Alternatively, these oxides and other oxides (with the metals in different oxidation states) can be produced by heating the corresponding hydroxides, carbonates, or oxalates in an inert atmosphere. Iron(II) oxide can be prepared by heating iron(II) oxalate, and cobalt(II) oxide is produced by heating cobalt(II) hydroxide:

$$\mathrm{FeC_2O_4}(s) \longrightarrow \mathrm{FeO}(s) + \mathrm{CO}(g) + \mathrm{CO_2}(g)$$

$$\mathrm{Co(OH)_2}(s) \longrightarrow \mathrm{CoO}(s) + \mathrm{H_2O}(g)$$

With the exception of CrO_3 and Mn_2O_7, transition metal oxides are not soluble in water. They can react with acids and, in a few cases, with bases. Overall, oxides of transition metals with the lowest oxidation states are basic (and react with acids), the intermediate ones are amphoteric, and the highest oxidation states are primarily acidic. Basic metal oxides at a low oxidation state react with aqueous acids to form solutions of salts and water. Examples include the reaction of cobalt(II) oxide accepting protons from nitric acid, and scandium(III) oxide accepting protons from hydrochloric acid:

$$\mathrm{CoO}(s) + 2\,\mathrm{HNO_3}(aq) \longrightarrow \mathrm{Co(NO_3)_2}(aq) + \mathrm{H_2O}(l)$$

$$\mathrm{Sc_2O_3}(s) + 6\,\mathrm{HCl}(aq) \longrightarrow 2\,\mathrm{ScCl_3}(aq) + 3\,\mathrm{H_2O}(l)$$

The oxides of metals with oxidation states of 4+ are amphoteric, and most are not soluble in either acids or bases. Vanadium(V) oxide, chromium(VI) oxide, and manganese(VII) oxide are acidic. They react with solutions of hydroxides to form salts of the oxyanions $\mathrm{VO_4^{3-}}$, $\mathrm{CrO_4^{2-}}$, and $\mathrm{MnO_4^-}$. For example, the complete ionic equation for the reaction of chromium(VI) oxide with a strong base is given by:

$$\mathrm{CrO_3}(s) + 2\,\mathrm{Na^+}(aq) + 2\,\mathrm{OH^-}(aq) \longrightarrow 2\,\mathrm{Na^+}(aq) + \mathrm{CrO_4^{2-}}(aq) + \mathrm{H_2O}(l)$$

Chromium(VI) oxide and manganese(VII) oxide react with water to form the acids H_2CrO_4 and $HMnO_4$, respectively.

Hydroxides

When a soluble hydroxide is added to an aqueous solution of a salt of a transition metal of the first transition series, a gelatinous precipitate forms. For example, adding a solution of sodium hydroxide to a solution of cobalt sulfate produces a gelatinous pink or blue precipitate of cobalt(II) hydroxide. The net ionic equation is:

$$\mathrm{Co^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{Co(OH)_2}(s)$$

In this and many other cases, these precipitates are hydroxides containing the transition metal ion, hydroxide ions, and water coordinated to the transition metal. In other cases, the precipitates are hydrated oxides composed of the metal ion, oxide ions, and water of hydration:

$$4\,\mathrm{Fe^{3+}}(aq) + 6\,\mathrm{OH^-}(aq) + n\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{Fe_2O_3 \cdot (n+3)H_2O}(s)$$

These substances do not contain hydroxide ions. However, both the hydroxides and the hydrated oxides react with acids to form salts and water. When precipitating a metal from solution, it is necessary to avoid an excess of hydroxide ion, as this may lead to complex ion formation as discussed later in this chapter. The precipitated metal hydroxides can be separated for further processing or for waste disposal.

Carbonates

Many of the elements of the first transition series form insoluble carbonates. It is possible to prepare these carbonates by the addition of a soluble carbonate salt to a solution of a transition metal salt. For example, nickel carbonate can be prepared from solutions of nickel nitrate and sodium carbonate according to the following net ionic equation:

$$\mathrm{Ni^{2+}}(aq) + \mathrm{CO_3{}^{2-}} \longrightarrow \mathrm{NiCO_3}(s)$$

The reactions of the transition metal carbonates are similar to those of the active metal carbonates. They react with acids to form metals salts, carbon dioxide, and water. Upon heating, they decompose, forming the transition metal oxides.

Other Salts

In many respects, the chemical behavior of the elements of the first transition series is very similar to that of the main group metals. In particular, the same types of reactions that are used to prepare salts of the main group metals can be used to prepare simple ionic salts of these elements.

A variety of salts can be prepared from metals that are more active than hydrogen by reaction with the corresponding acids: Scandium metal reacts with hydrobromic acid to form a solution of scandium bromide:

$$2\,\mathrm{Sc}(s) + 6\,\mathrm{HBr}(aq) \longrightarrow 2\,\mathrm{ScBr_3}(aq) + 3\,\mathrm{H_2}(g)$$

The common compounds that we have just discussed can also be used to prepare salts. The reactions involved include the reactions of oxides, hydroxides, or carbonates with acids. For example:

$$\mathrm{Ni(OH)_2}(s) + 2\,\mathrm{H_3O^+}(aq) + 2\,\mathrm{ClO_4{}^-}(aq) \longrightarrow \mathrm{Ni^{2+}}(aq) + 2\,\mathrm{ClO_4{}^-}(aq) + 4\,\mathrm{H_2O}(l)$$

Substitution reactions involving soluble salts may be used to prepare insoluble salts. For example:

$$\mathrm{Ba^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{K^+}(aq) + \mathrm{CrO_4{}^{2-}}(aq) \longrightarrow \mathrm{BaCrO_4}(s) + 2\,\mathrm{K^+}(aq) + 2\,\mathrm{Cl^-}(aq)$$

In our discussion of oxides in this section, we have seen that reactions of the covalent oxides of the transition elements with hydroxides form salts that contain oxyanions of the transition elements.

High Temperature Superconductors

A superconductor is a substance that conducts electricity with no resistance. This lack of resistance means that there is no energy loss during the transmission of electricity. This would lead to a significant reduction in the cost of electricity.

Most currently used, commercial superconducting materials, such as NbTi and Nb_3Sn, do not become superconducting until they are cooled below 23 K (−250 °C). This requires the use of liquid helium, which has a boiling temperature of 4 K and is expensive and difficult to handle. The cost of liquid helium has deterred the widespread application of superconductors.

One of the most exciting scientific discoveries of the 1980s was the characterization of compounds that exhibit superconductivity at temperatures above 90 K. (Compared to liquid helium, 90 K is a high temperature.) Typical among the high-temperature superconducting materials are oxides containing yttrium (or one of several rare earth elements), barium, and copper in a 1:2:3 ratio. The formula of the ionic yttrium compound is $YBa_2Cu_3O_7$.

The new materials become superconducting at temperatures close to 90 K (Figure 23.2.10), temperatures that can be reached by cooling with liquid nitrogen (boiling temperature of 77 K). Not only are liquid nitrogen-cooled materials easier to handle, but the cooling costs are also about 1000 times lower than for liquid helium.

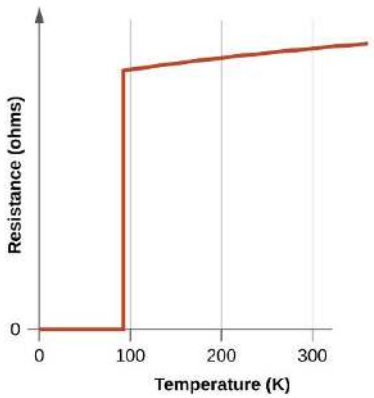


Figure 23.2.10: The resistance of the high-temperature superconductor $YBa_2Cu_3O_7$ varies with temperature. Note how the resistance falls to zero below 92 K, when the substance becomes superconducting.

A graph of resistance (ohms) against temperature (Kelvin) is shown. The line remains constant at 0 ohms up until 92 Kelvin in which there is a sharp increase in resistance which continues increasing with a low slope.

Although the brittle, fragile nature of these materials presently hampers their commercial applications, they have tremendous potential that researchers are hard at work improving their processes to help realize. Superconducting transmission lines would carry current for hundreds of miles with no loss of power due to resistance in the wires. This could allow generating stations to be located in areas remote from population centers and near the natural resources necessary for power production. The first project demonstrating the viability of high-temperature superconductor power transmission was established in New York in 2008.



Figure 23.2.11: (a) This magnetic levitation train (or maglev) uses superconductor technology to move along its tracks. (b) A magnet can be levitated using a dish like this as a superconductor. (credit a: modification of work by Alex Needham; credit b: modification of work by Kevin Jarrett)

A. a white train is on a track with a building standing on a bed of water in the background. B. A magnet is floating in a dish with frost emerging from the dish.

Researchers are also working on using this technology to develop other applications, such as smaller and more powerful microchips. In addition, high-temperature superconductors can be used to generate magnetic fields for applications such as medical devices, magnetic levitation trains, and containment fields for nuclear fusion reactors (Figure 23.2.11).



Video 23.2.1: Watch how a high-temperature superconductor levitates around a magnetic racetrack in the video.

Summary

The transition metals are elements with partially filled *d* orbitals, located in the *d*-block of the periodic table. The reactivity of the transition elements varies widely from very active metals such as scandium and iron to almost inert elements, such as the platinum metals. The type of chemistry used in the isolation of the elements from their ores depends upon the concentration of the element in its ore and the difficulty of reducing ions of the elements to the metals. Metals that are more active are more difficult to reduce.

Transition metals exhibit chemical behavior typical of metals. For example, they oxidize in air upon heating and react with elemental halogens to form halides. Those elements that lie above hydrogen in the activity series react with acids, producing salts and hydrogen gas. Oxides, hydroxides, and carbonates of transition metal compounds in low oxidation states are basic. Halides and other salts are generally stable in water, although oxygen must be excluded in some cases. Most transition metals form a variety of stable oxidation states, allowing them to demonstrate a wide range of chemical reactivity.

Glossary

actinide series
(also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

coordination compound
stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

***d*-block element**
one of the elements in groups 3–11 with valence electrons in *d* orbitals

***f*-block element**
(also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

first transition series
transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

fourth transition series
transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

hydrometallurgy
process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

lanthanide series

(also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

platinum metals

group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

rare earth element

collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

second transition series

transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

smelting

process of extracting a pure metal from a molten ore

steel

material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

superconductor

material that conducts electricity with no resistance

third transition series

transition elements in the sixth period of the periodic table (third row of the *d*-block), atomic numbers 57 and 72–79

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23.3: Coordination Compounds

Learning Objectives

- List the defining traits of coordination compounds
- Describe the structures of complexes containing monodentate and polydentate ligands
- Use standard nomenclature rules to name coordination compounds
- Explain and provide examples of geometric and optical isomerism
- Identify several natural and technological occurrences of coordination compounds

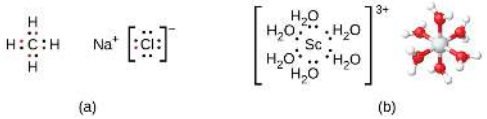
The hemoglobin in your blood, the chlorophyll in green plants, vitamin B_{12}, and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored (Figure 23.3.1). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.



Figure 23.3.1: Metal ions that contain partially filled d subshell usually form colored complex ions; ions with empty d subshell (d^0) or with filled d subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with M = Sc^{3+}(d^0), Cr^{3+}(d^3), Co^{2+}(d^7), Ni^{2+}(d^8), Cu^{2+}(d^9), and Zn^{2+}(d^{10}). (credit: Sahar Atwa)

There are six containers that are each filled with a different color liquid. The first is clear, followed by purple, red, teal, blue, and the last one is also clear.

Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4. The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit NaCl (Figure 23.3.2). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a central metal ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form coordination compounds. The Lewis base donors, called ligands, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a donor atom with a lone pair of electrons that can form a coordinate bond to the metal.



(a) (b)

Figure 23.3.2: (a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)

The coordination sphere consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The coordination number of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two (Figure 23.3.3). For the copper(II) ion in $[CuCl_4]^{2-}$, the coordination number is four, whereas for the cobalt(II) ion in $[Co(H_2O)_6]^{2+}$ the coordination number is six. Each of these ligands is monodentate, from the Greek for "one toothed," meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.

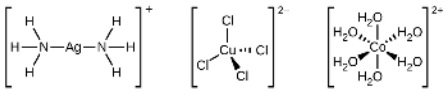
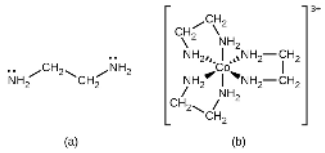


Figure 23.3.3: The complexes (a) $[Ag(NH_3)_2]^+$, (b) $[Cu(Cl)_4]^{2-}$, and (c) $[Co(H_2O)_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.

The structural formulas for Ag N H 3 subscript 2, C u C l subscript 4, and C o H 2 O subscript 6 is shown in enclosing brackets showing their individual charges on the top right of positive 1, negative 2 and positive 2 respectively.

Many other ligands coordinate to the metal in more complex fashions. Bidentate ligands are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base (Figure 23.3.4). Both of the atoms can coordinate to a single metal center. In the complex $[Co(en)_3]^{3+}$, there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.



(a) (b)

Figure 23.3.4: (a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex $[Co(en)_3]^{3+}$ *contains three of these ligands, each forming two bonds to the cobalt ion.*

Any ligand that bonds to a central metal ion by more than one donor atom is a polydentate ligand (or "many teeth") because it can bite into the metal center with more than one bond. The term chelate (pronounced "KEY-late") from the Greek for "claw" is also used to describe this type of interaction. Many polydentate ligands are chelating ligands, and a complex consisting of one or more of these ligands and a central metal is a chelate. A chelating ligand is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab's claw would hold a marble. Figure 23.3.4 showed one example of a chelate and the heme complex in hemoglobin is another important example (Figure 23.3.5). It contains a polydentate ligand with four donor atoms that coordinate to iron.

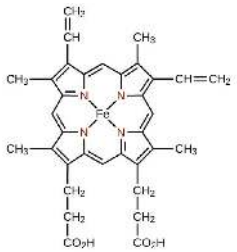


Figure 23.3.5: The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.

Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3, Cl^-, and H_2O, are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $H_2NCH_2CH_2NH_2$, and the anion of the acid glycine, $NH_2CH_2CO_2^-$ (Figure 23.3.6) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The heme ligand (Figure 23.3.5) is a tetradentate ligand.

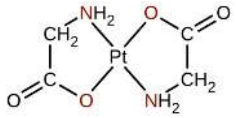


Figure 23.3.6: Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.

The Naming of Complexes

The nomenclature of the complexes is patterned after a system suggested by Alfred Werner, a Swiss chemist and Nobel laureate, whose outstanding work more than 100 years ago laid the foundation for a clearer understanding of these compounds. The following five rules are used for naming complexes:

1. If a coordination compound is ionic, name the cation first and the anion second, in accordance with the usual nomenclature.
2. Name the ligands first, followed by the central metal. Name the ligands alphabetically. Negative ligands (anions) have names formed by adding *-o* to the stem name of the group (e.g., Table 23.3.1. For most neutral ligands, the name of the molecule is used. The four common exceptions are *aqua* (H_2O), *amine* (NH_3), *carbonyl* (CO), and *nitrosyl* (NO). For example, name $[Pt(NH_3)_2Cl_4]$ as diaminetetrachloroplatinum(IV).
3. If more than one ligand of a given type is present, the number is indicated by the prefixes *di-* (for two), *tri-* (for three), *tetra-* (for four), *penta-* (for five), and *hexa-* (for six). Sometimes, the prefixes *bis-* (for two), *tris-* (for three), and *tetrakis-* (for four) are used when the name of the ligand already includes *di-*, *tri-*, or *tetra-*, or when the ligand name begins with a vowel. For example, the ion bis(bipyridyl)osmium(II) uses bis- to signify that there are two ligands attached to Os, and each bipyridyl ligand contains two pyridine groups (C_5H_4N).

Table 23.3.1: Examples of Anionic Ligands

Anionic Ligand	Name
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
CN^-	cyano
NO_3^-	nitrato
OH^-	hydroxo
O^{2-}	oxo
$C_2O_4^{2-}$	oxalato
CO_2^{2-}	carbonato

When the complex is either a cation or a neutral molecule, the name of the central metal atom is spelled exactly like the name of the element and is followed by a Roman numeral in parentheses to indicate its oxidation state (Tables 23.3.2, 23.3.3, and 23.3.3). When the complex is an anion, the suffix -ate is added to the stem of the name of the metal, followed by the Roman numeral designation of its oxidation state.

Table 23.3.2: Select Coordination Complexes based on total Charge

Examples in Which the Complex Is Cation	
$[Co(NH_3)_6]Cl_3$	hexaaminecobalt(III) chloride
$[Pt(NH_3)_4Cl_2]^{2+}$	tetraaminedichloroplatinum(IV) ion
$[Ag(NH_3)_2]^+$	diaminesilver(I) ion
$[Cr(H_2O)_4Cl_2]Cl$	tetraaquadichlorochromium(III) chloride
$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulfate
Examples in Which the Complex Is Neutral	
$[Pt(NH_3)_2Cl_4]$	diaminetetrachloroplatinum(IV)
$[Ni(H_2NCH_2CH_2NH_2)_2Cl_2]$	dichlorobis(ethylenediamine)nickel(II)
Examples in Which the Complex Is an Anion	
$[PtCl_6]^{2-}$	hexachloroplatinate(IV) ion
$Na_2[SnCl_6]$	sodium hexachlorostannate(IV)

Sometimes, the Latin name of the metal is used when the English name is clumsy. For example, *ferrate* is used instead of *ironate*, *plumbate* instead *leadate*, and *stannate* instead of *tinate*. The oxidation state of the metal is determined based on the charges of each ligand and the overall charge of the coordination compound. For example, in $[Cr(H_2O)_4Cl_2]Br$, the coordination sphere (in brackets) has a charge of 1+ to balance the bromide ion. The water ligands are neutral, and the chloride ligands are anionic with a charge of 1− each. To determine the oxidation state of the metal, we set the overall charge equal to the sum of the ligands and the metal: $+1 = -2 + x$, so the oxidation state (x) is equal to 3+.

Example 23.3.1: Coordination Numbers and Oxidation States

Determine the name of the following complexes and give the coordination number of the central metal atom.

a. $Na_2[PtCl_6]$
b. $K_3[Fe(C_2O_4)_3]$
c. $[Co(NH_3)_5Cl]Cl_2$

Solution

a. There are two Na^+ ions, so the coordination sphere has a negative two charge: $[PtCl_6]^{2-}$. There are six anionic chloride ligands, so $-2 = -6 + x$, and the oxidation state of the platinum is 4+. The name of the complex is sodium hexachloroplatinate(IV), and the coordination number is six.
b. The coordination sphere has a charge of 3− (based on the potassium) and the oxalate ligands each have a charge of 2−, so the metal oxidation state is given by $-3 = -6 + x$, and this is an iron(III) complex. The name is potassium trisoxalatoferrate(III) (note that tris is used instead of tri because the ligand name starts with a vowel). Because oxalate is a bidentate ligand, this complex has a coordination number of six.
c. In this example, the coordination sphere has a cationic charge of 2+. The NH_3 ligand is neutral, but the chloro ligand has a charge of 1−. The oxidation state is found by $+2 = -1 + x$ and is 3+, so the complex is pentaaminechlorocobalt(III) chloride and the coordination number is six.

Exercise 23.3.1

The complex potassium dicyanoargenate(I) is used to make antiseptic compounds. Give the formula and coordination number.

Answer

$K[Ag(CN)_2]$; coordination number two

The Structures of Complexes

The most common structures of the complexes in coordination compounds are octahedral, tetrahedral, and square planar (Figure 23.3.7). For transition metal complexes, the coordination number determines the geometry around the central metal ion. Table 23.3.3 compares coordination numbers to the molecular geometry:

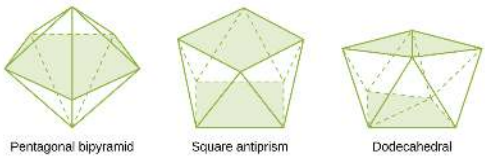


Figure 23.3.7: These are geometries of some complexes with coordination numbers of seven and eight.

Table 23.3.3: Coordination Numbers and Molecular Geometry

Coordination Number	Molecular Geometry	Example
2	linear	$[Ag(NH_3)_2]^+$
3	trigonal planar	$[Cu(CN)_3]^{2-}$
4	tetrahedral(d^0 or d^{10}), low oxidation states for M	$[Ni(CO)_4]$
4	square planar (d^8)	$[NiCl_4]^{2-}$
5	trigonal bipyramidal	$[CoCl_5]^{2-}$
5	square pyramidal	$[VO(CN)_4]^{2-}$
6	octahedral	$[CoCl_6]^{3-}$
7	pentagonal bipyramid	$[ZrF_7]^{3-}$
8	square antiprism	$[ReF_8]^{2-}$
8	dodecahedron	$[Mo(CN)_8]^{4-}$
9 and above	more complicated structures	$[ReH_9]^{2-}$

Unlike main group atoms in which both the bonding and nonbonding electrons determine the molecular shape, the nonbonding *d*-electrons do not change the arrangement of the ligands. Octahedral complexes have a coordination number of six, and the six donor atoms are arranged at the corners of an octahedron around the central metal ion. Examples are shown in Figure 23.3.8. The chloride and nitrate anions in $[Co(H_2O)_6]Cl_2$ and $[Cr(en)_3](NO_3)_3$, and the potassium cations in $K_2[PtCl_6]$, are outside the brackets and are not bonded to the metal ion.

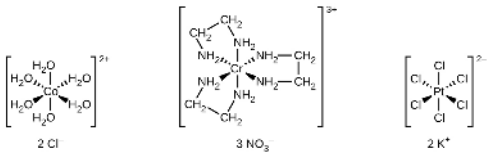
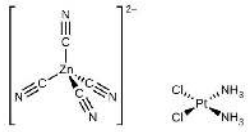


Figure 23.3.8: Many transition metal complexes adopt octahedral geometries, with six donor atoms forming bond angles of 90° about the central atom with adjacent ligands. Note that only ligands within the coordination sphere affect the geometry around the metal center.

The structural formulas for C o H 2 O subscript 6, C r e n subscript 3, and P t c l subscript 6 is shown in enclosing brackets showing their individual charges on the top right. These charges are positive 2, positive 3 and negative 2 respectively. 2 chloride ions, 3 nitrate ions, and 2 potassium ions are shown outside of the three brackets respectively.

For transition metals with a coordination number of four, two different geometries are possible: tetrahedral or square planar. Unlike main group elements, where these geometries can be predicted from VSEPR theory, a more detailed discussion of transition metal orbitals (discussed in the section on Crystal Field Theory) is required to predict which complexes will be tetrahedral and which

will be square planar. In tetrahedral complexes such as $[Zn(CN)_4]^{2-}$ (Figure 23.3.9), each of the ligand pairs forms an angle of 109.5°. In square planar complexes, such as $[Pt(NH_3)_2Cl_2]$, each ligand has two other ligands at 90° angles (called the *cis* positions) and one additional ligand at an 180° angle, in the *trans* position.



(a) (b)

Figure 23.3.9: Transition metals with a coordination number of four can adopt a tetrahedral geometry (a) as in $K_2[Zn(CN)_4]$ or a square planar geometry (b) as shown in $[Pt(NH_3)_2Cl_2]$. Structural formulas of K subscript 2 Z n C N subscript 4 and P t N H subscript 3 subscript 2 C l subscript 2 are shown with wedge and dashed lines to show a more three dimensional structure.

Isomerism in Complexes

Isomers are different chemical species that have the same chemical formula. Transition metals often form **geometric isomers**, in which the same atoms are connected through the same types of bonds but with differences in their orientation in space. Coordination complexes with two different ligands in the *cis* and *trans* positions from a ligand of interest form isomers. For example, the octahedral $[Co(NH_3)_4Cl_2]^+$ ion has two isomers. In the *cis* configuration, the two chloride ligands are adjacent to each other (Figure 23.3.1). The other isomer, the *trans* configuration, has the two chloride ligands directly across from one another.

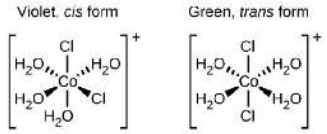


Figure 23.3.10: The cis and trans isomers of $[Co(H_2O)_4Cl_2]^+$ contain the same ligands attached to the same metal ion, but the spatial arrangement causes these two compounds to have very different properties.

For the Violet, cis form the two chlorine is adjacent to one another. For the green, trans form, the two chlorine is opposite from one another.

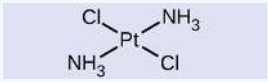
Different geometric isomers of a substance are different chemical compounds. They exhibit different properties, even though they have the same formula. For example, the two isomers of $[Co(NH_3)_4Cl_2]NO_3$ differ in color; the *cis* form is violet, and the *trans* form is green. Furthermore, these isomers have different dipole moments, solubilities, and reactivities. As an example of how the arrangement in space can influence the molecular properties, consider the polarity of the two $[Co(NH_3)_4Cl_2]NO_3$ isomers. Remember that the polarity of a molecule or ion is determined by the bond dipoles (which are due to the difference in electronegativity of the bonding atoms) and their arrangement in space. In one isomer, *cis* chloride ligands cause more electron density on one side of the molecule than on the other, making it polar. For the *trans* isomer, each ligand is directly across from an identical ligand, so the bond dipoles cancel out, and the molecule is nonpolar.

Example 23.3.2: Geometric Isomers

Identify which geometric isomer of $[Pt(NH_3)_2Cl_2]$ is shown in Figure 23.3.9b. Draw the other geometric isomer and give its full name.

Solution

In the Figure 23.3.9b, the two chlorine ligands occupy *cis* positions. The other form is shown in below. When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diaminedichloroplatinum(II).



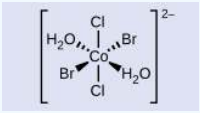
Structural formula of trans-diaminedichloroplatinum(II). The chlorine atoms are opposite each other in the same plane. This is also the case for the two amines.

The *trans* isomer of $[Pt(NH_3)_2Cl_2]$ has each ligand directly across from an adjacent ligand.

Exercise 23.3.2

Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).

Answer



Cobalt is located at the center with the left and right wedges connected to bromine and H 2 O respectively. The left and right dash lines are connected to H 2 O and bromine respectively. Pointing directly upwards and downwards opposite from one another are the chlorine. The entire structural formula is enclosed in square bracket with a superscript of 2 negative.

Another important type of isomers are optical isomers, or enantiomers, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as $[M(en)_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in Figure 23.3.11. These two isomers will react differently with other optical isomers. For example, DNA helices are optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.

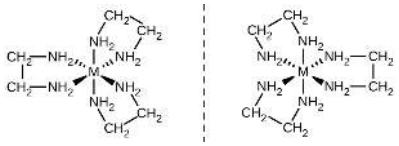


Figure 23.3.11: The complex $[M(en)_3]^{n+}$ (M^{n+} = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.

Two structural formulas of open bracket M e n subscript 3 close bracket superscript n positive are shown as mirror images with the dashed vertical line in the center as the mirror plane.

The $[Co(en)_2Cl_2]^+$ ion exhibits geometric isomerism (*cis*/*trans*), and its *cis* isomer exists as a pair of optical isomers (Figure 23.3.12).



Figure 23.3.12: Three isomeric forms of $[Co(en)_2Cl_2]^+$ exist. The trans isomer, formed when the chlorines are positioned at a 180° angle, has very different properties from the cis isomers. The mirror images of the cis isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.

For the cis isomers, the structural formula shown are mirror images of one another. The two chlorine atoms are adjacent to one another in each cis structure. The trans form is also shown with the chlorine directly opposite from one another.

Linkage isomers occur when the coordination compound contains a ligand that can bind to the transition metal center through two different atoms. For example, the CN ligand can bind through the carbon atom (cyano) or through the nitrogen atom (isocyano). Similarly, SCN− can be bound through the sulfur or nitrogen atom, affording two distinct compounds ($[Co(NH_3)_5SCN]^{2+}$ or $[Co(NH_3)_5NCS]^{2+}$).

Ionization isomers (or coordination isomers) occur when one anionic ligand in the inner coordination sphere is replaced with the counter ion from the outer coordination sphere. A simple example of two ionization isomers are $[CoCl_6][Br]$ and $[CoCl_5Br][Cl]$.

Coordination Complexes in Nature and Technology

Chlorophyll, the green pigment in plants, is a complex that contains magnesium (Figure 23.3.13). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

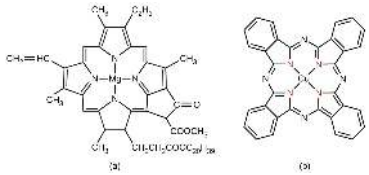


Figure 23.3.13: (a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center. (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.

Transition Metal Catalysts

One of the most important applications of transition metals is as industrial catalysts. As you recall from the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (Figure 23.3.14). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.



Figure 23.3.14: (a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by “Mr. Brian”/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by “osseous”/Flickr)

Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from Figure 23.3.13) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme (Figure 23.3.15), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is Fe^{2+}; oxidation of the iron to Fe^{3+} prevents oxygen transport.

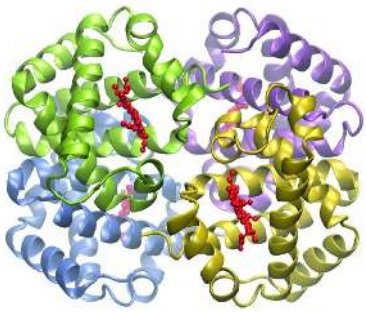


Figure 23.3.15: Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.

Three dimensional structure of hemoglobin has many ribbon like structures forming helices and are entangled with one another in a disordered manner. The four subunits are colored differently. Around the center of hemoglobin are multiple linear structures composed of red globules.

Complexing agents often are used for water softening because they tie up such ions as Ca^{2+}, Mg^{2+}, and Fe^{2+}, which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, coordinates to metal ions through six donor atoms and prevents the metals from reacting (Figure 23.3.16). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

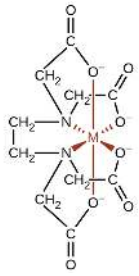


Figure 23.3.16: The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.

Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL), $HSCH_2CH(SH)CH_2OH$, is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate (Figure 23.3.17). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering from blood diseases such as Cooley's anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.

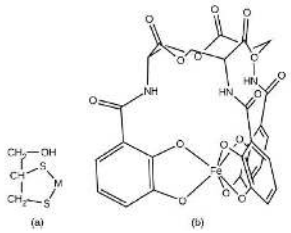


Figure 23.3.17: Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.

Example 23.3.3: Chelation Therapy

Ligands like BAL and enterobactin are important in medical treatments for heavy metal poisoning. However, chelation therapies can disrupt the normal concentration of ions in the body, leading to serious side effects, so researchers are searching for new chelation drugs. One drug that has been developed is dimercaptosuccinic acid (DMSA), shown in Figure 23.3.18. Identify which atoms in this molecule could act as donor atoms.



DMSA
is shown with all of the lone pairs on O and S drawn out. " style="width: 650px; height: 191px;" width="650px" height="191px" data-cke-saved-src="/@api/deki/files/65922/
CNX
_Chem_19_02_DMSA.jpg" src="/@api/deki/files/65922/CNX_Chem_19_02_DMSA.jpg" data-quail-id="607">

Figure 23.3.18: Dimercaptosuccinic acid is used to treat heavy metal poisoning.

Solution

All of the oxygen and sulfur atoms have lone pairs of electrons that can be used to coordinate to a metal center, so there are six possible donor atoms. Geometrically, only two of these atoms can be coordinated to a metal at once. The most common binding mode involves the coordination of one sulfur atom and one oxygen atom, forming a five-member ring with the metal.

Exercise 23.3.3

Some alternative medicine practitioners recommend chelation treatments for ailments that are not clearly related to heavy metals, such as cancer and autism, although the practice is discouraged by many scientific organizations.[1] Identify at least two biologically important metals that could be disrupted by chelation therapy.

Answer

Ca, Fe, Zn, and Cu

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diaminedichloroplatinum(II), $[Pt(NH_3)_2(Cl)_2]$, and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diamine $(NH_3)_2$ portion is retained with other groups, replacing the dichloro $[(Cl)_2]$ portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

Summary

The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by coordinate covalent bonds. Ligands with more than one donor atom are called polydentate ligands and form chelates. The common geometries found in complexes are tetrahedral and square planar (both with a coordination number of four) and octahedral (with a coordination number of six). *Cis* and *trans* configurations are possible in some octahedral and square planar complexes. In addition to these geometrical isomers, optical isomers (molecules or ions that are mirror images but not superimposable) are possible in certain octahedral complexes. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use.

Footnotes

1. National Council against Health Fraud, *NCAHF Policy Statement on Chelation Therapy*, (Peabody, MA, 2002).

Glossary

bidentate ligand
ligand that coordinates to one central metal through coordinate bonds from two different atoms

central metal
ion or atom to which one or more ligands is attached through coordinate covalent bonds

chelate
complex formed from a polydentate ligand attached to a central metal

chelating ligand
ligand that attaches to a central metal ion by bonds from two or more donor atoms

***cis* configuration**
configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

coordination compound
substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

coordination number
number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

coordination sphere
central metal atom or ion plus the attached ligands of a complex

donor atom
atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

ionization isomer
(or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

ligand
ion or neutral molecule attached to the central metal ion in a coordination compound

linkage isomer
coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

monodentate
ligand that attaches to a central metal through just one coordinate covalent bond

optical isomer
(also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

polydentate ligand
ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

***trans* configuration**
configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

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23.4: Structure and Isomerization

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

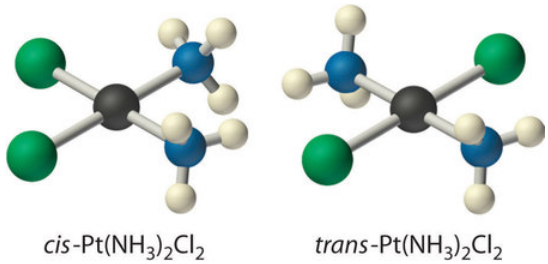


Figure 23.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases. For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced,

and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

? Exercise 23.4.1

Draw the cis and trans isomers of the following compounds:

a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

? Exercise 23.4.2

Only one isomer of (tmeda)$PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

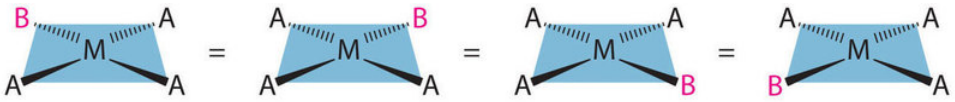
Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:

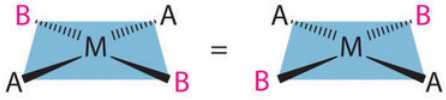


MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:



MA_2B_2 square planar complex, *cis* isomer

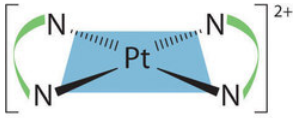


MA_2B_2 square planar complex, *trans* isomer

Figure 23.4.1).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

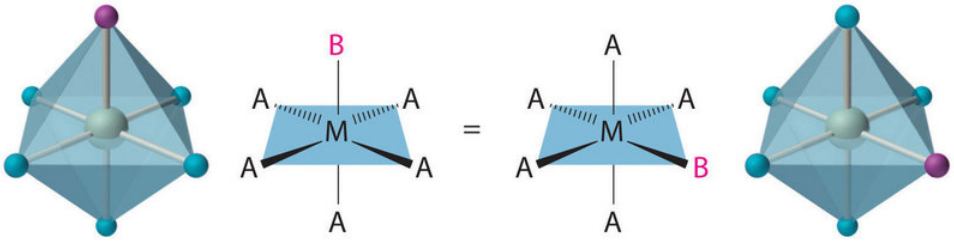
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

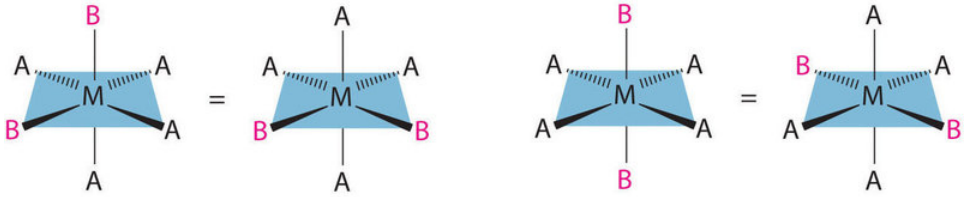
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



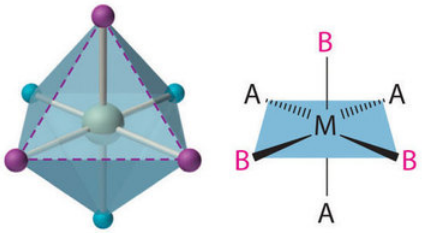
MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:

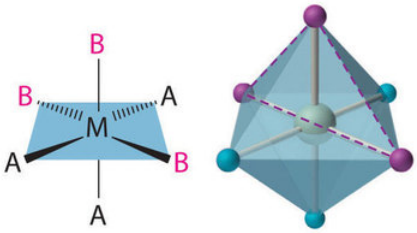


MA_4B_2 octahedral complex, *cis* isomer **MA_4B_2 octahedral complex, *trans* isomer**

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer



MA_3B_3 octahedral complex, *mer* isomer

Example 23.4.1

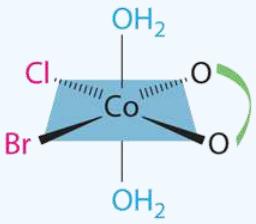
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

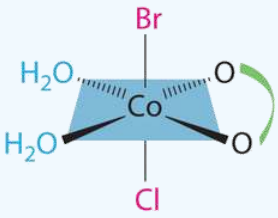
Asked for: structures of geometrical isomers

Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:

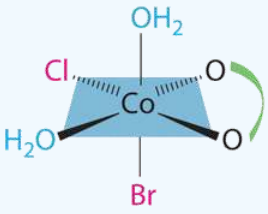


H_2O's *trans*

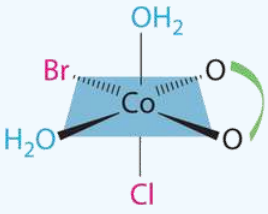


Br, Cl *trans*

In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



H_2O's *cis*; Br, Cl *cis*; Cl *trans* to O



H_2O's *cis*; Br, Cl *cis*; Br *trans* to O

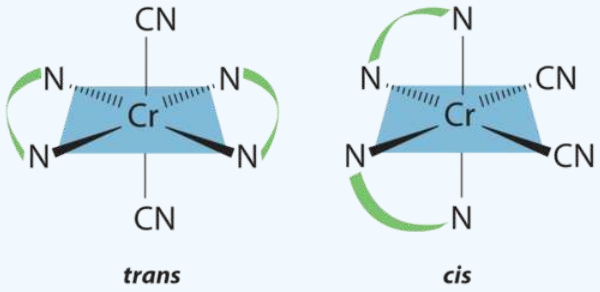
This complex can therefore exist as four different geometrical isomers.

Exercise 23.4.1

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer

Two geometrical isomers are possible: trans and cis.



Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

Contributors and Attributions

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23.5: Bonding in Coordinate Compounds

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure $23.5.1a$). 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 $23.5.1b$, 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.

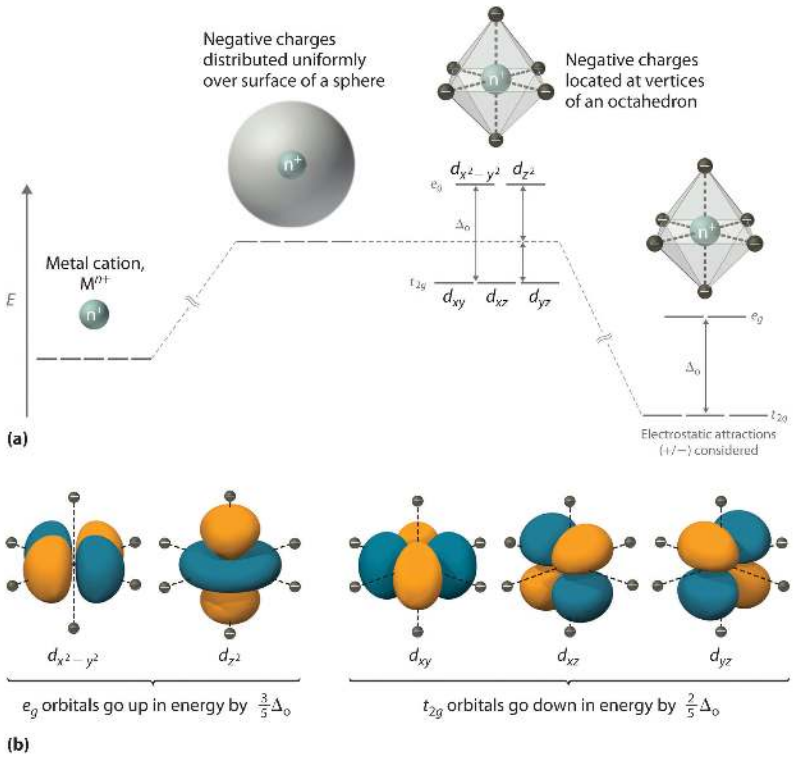


Figure 23.5.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase 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.

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.$$

> *Crystal field splitting does not change the total energy of the d orbitals.*

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 23.5.1*a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 23.5.1 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 24.6.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins

parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

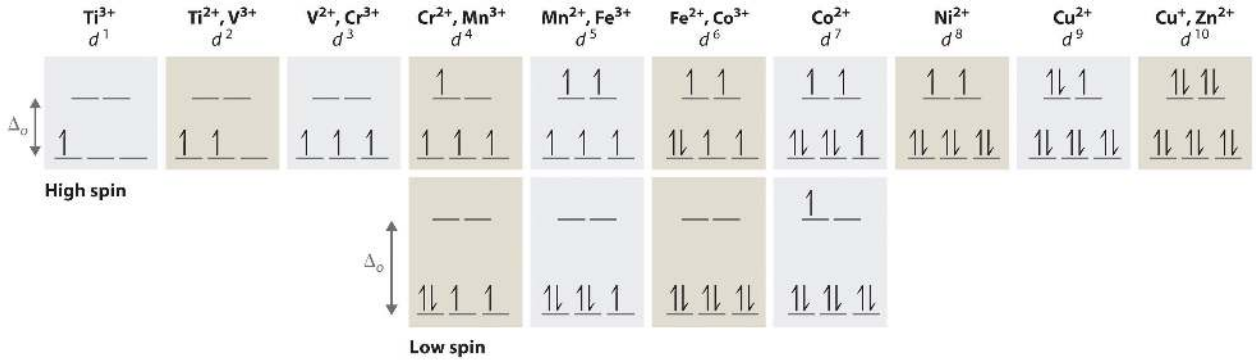


Figure 23.5.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 23.5.1.

Table 23.5.1: 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
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I-$ because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{CO \approx CN^- > NO_2^-} > en > NH_3 > \underset{\text{intermediate-field ligands}}{SCN^- > H_2O > oxalate^{2-} > OH^- > F} > acetate^- > \underset{\text{weak-field ligands}}{Cl^- > Br^- > I^-}$$

The values of Δ_o listed in Table 23.5.1 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.*

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition (Figure 24.6.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o.

Figure 23.5.3: A d–d Transition. In a d–d transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 23.5.2 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 23.5.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

Example 23.5.1

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 23.5.1

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. $[PtCl_4]^{2-}$

Answers

a. octahedral; high spin; five
b. square planar; low spin; no unpaired electrons

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

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23.6: Applications of Coordination Compounds

Chelating Agents for Poising (EDTA)

Biomolecules (Porphorins and Hemoglogin)

Drugs and Health (cis-Platin)

Learning Objectives

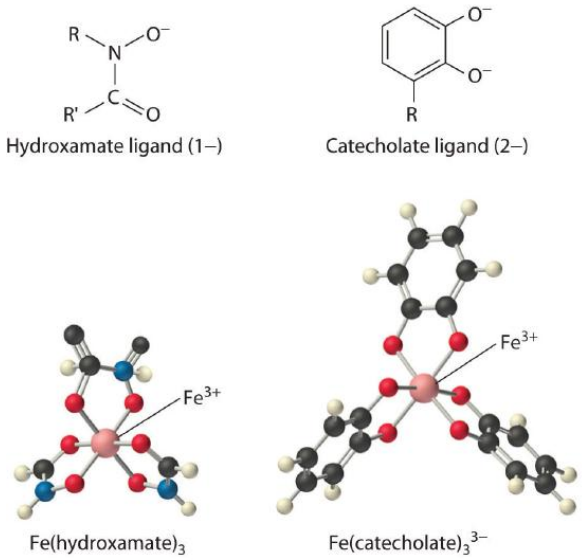
- To become familiar with some of the roles of transition-metal complexes in biological systems.

In this section, we describe several systems that illustrate the roles transition metals play in biological systems. Our goal is for you to understand why the chemical properties of these elements make them essential for life. We begin with a discussion of the strategies organisms use to extract transition metals from their environment. The section continues with a brief discussion of the use of transition metals in reactions that involve the transfer of electrons, reactions of small molecules such as O_2, Lewis-acid catalysis, and the generation of reactive organic radicals.

Uptake and Storage of Transition Metals

There are three possible dietary levels for any essential element: deficient, optimal, and toxic, in order of increasing concentration in the diet. If the concentration of an essential element in the diet is too low, an organism must be able to extract the element from the environment and concentrate it. If the concentration of an essential element in the diet is too high, an organism must be able to limit its intake to avoid toxic effects. Moreover, organisms must be able to switch off the uptake process rapidly if dietary levels rise suddenly, and they must be able to store essential elements for future use.

Three distinct steps are involved in transition metal uptake. First, the metal must be “mobilized” from the environment and brought into contact with a cell in a form that can be absorbed. Second, the metal must be transported across the cell membrane into the cell. Third, the element must be transported to its point of utilization within a cell or to other cells within the organism. In our discussion, we focus on the uptake, transport, and storage of iron, which illustrates the most important points. Because iron deficiency (anemia) is the most widespread nutritional deficiency known in humans, the uptake of iron is especially well understood.



Iron complexes in biological systems. Iron(III) forms very stable octahedral complexes with hydroxamate and catecholate ligands.

The solubility of metal ions such as Fe^{3+}, which form highly insoluble hydroxides, depends on the pH and the presence of complexing agents. In an oxygen-containing atmosphere, iron exists as Fe(III) because of the positive reduction potential of Fe^{3+} ($Fe^{3+} + e^- \rightarrow Fe^{2+}$; $E° = +0.77$ V). Because ferric hydroxide [$Fe(OH)_3$] is highly insoluble ($K_{sp} \approx 1 \times 10^{-39}$), the equilibrium

concentration of $Fe^{3+}(aq)$ at pH 7.0 is very low, about 10^{-18} M. You would have to drink 2×10^{13} L of iron-saturated water per day (roughly 5 mi^3) to consume the recommended daily intake of Fe for humans, which is about 1 mg/day. Animals such as humans can overcome this problem by consuming concentrated sources of iron, such as red meat, but microorganisms cannot.

Consequently, most microorganisms synthesize and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium. Siderophores are generally cyclic compounds that use bidentate ligands, such as the hydroxamate and catecholate groups shown here, to bind Fe^{3+} in an octahedral arrangement. Typical siderophores are ferrichrome, a cyclic peptide produced by fungi, and enterobactin, a cyclic ester produced by bacteria (Figure 23.6.1). Attaching the three iron ligands to a cyclic framework greatly increases the stability of the resulting Fe^{3+} complex due to the chelate effect described in Section 23.4. The formation constants for the Fe^{3+} complexes of ferrichrome and enterobactin are about 10^{32} and 10^{40}, respectively, which are high enough to allow them to dissolve almost any Fe(III) compound.

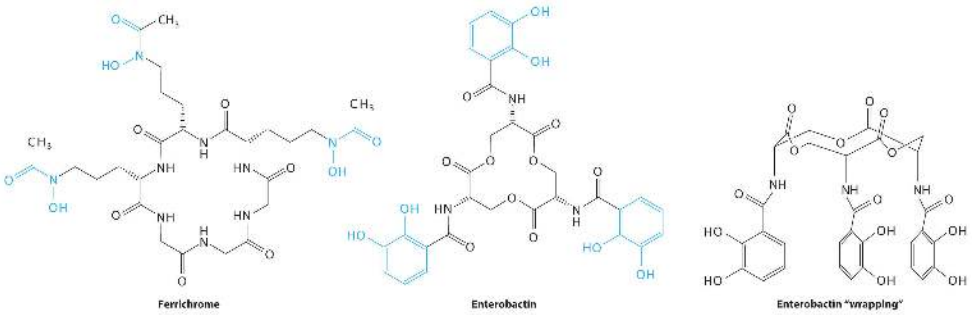


Figure 23.6.1: Siderophores. Ferrichrome (a) and enterobactin (b) are siderophores that use hydroxamate and catecholate ligands, respectively, to bind Fe^{3+}. The "wrapped" drawing of enterobactin (c) shows how the cyclic ester framework places the three catecholate ligands in the correct orientation to bind to a single Fe^{3+} ion, which is an application of the chelate effect. The actual structure of ferrichrome is similar to that of enterobactin, with the three hydroxamate ligands adjacent to one another for optimal binding of Fe^{3+}. Note: For clarity, most or all hydrogen atoms have been omitted in this and the following structures.

Siderophores increase the $[Fe^{3+}]$ in solution, providing the bacterium that synthesized them (as well as any competitors) with a supply of iron. In addition, siderophores neutralize the positive charge on the metal ion and provide a hydrophobic "wrapping" that enables the Fe^{3+}–siderophore complex to be recognized by a specific protein that transports it into the interior of a cell. Once it is inside a cell, the iron is reduced to Fe^{2+}, which has a much lower affinity for the siderophore and spontaneously dissociates.

In contrast, multicellular organisms can increase the concentration of iron in their diet by lowering the pH in the gastrointestinal tract. At pH 1.0 (the approximate pH of the stomach), most Fe(III) salts dissolve to form $Fe^{3+}(aq)$, which is absorbed by specific proteins in the intestinal wall. A protein called transferrin forms a complex with iron(III), allowing it to be transported to other cells. Proteins that bind tightly to Fe(III) can also be used as antibacterial agents because iron is absolutely essential for bacterial growth. For example, milk, tears, and egg white all contain proteins similar to transferrin, and their high affinity for Fe^{3+} allows them to sequester iron, thereby preventing bacteria from growing in these nutrient-rich media.

Iron is released from transferrin by reduction to Fe^{2+}, and then it is either used immediately (e.g., for the synthesis of hemoglobin) or stored in a very large protein called ferritin for future use (Figure 23.6.2). Ferritin uses oxygen to oxidize Fe^{2+} to Fe^{3+}, which at neutral pH precipitates in the central cavity of the protein as a polymeric mixture of $Fe(OH)_3$ and $FePO_4$. Because a fully loaded ferritin molecule can contain as many as 4500 Fe atoms, which corresponds to about 25% Fe by mass, ferritin is an effective way to store iron in a highly concentrated form. When iron is needed by a cell, the Fe^{3+} is reduced to the much more soluble Fe^{2+} by a reductant such as ascorbic acid (vitamin C). The structure of ferritin contains channels at the junctions of the subunits, which provide pathways for iron to enter and leave the interior of a molecule.

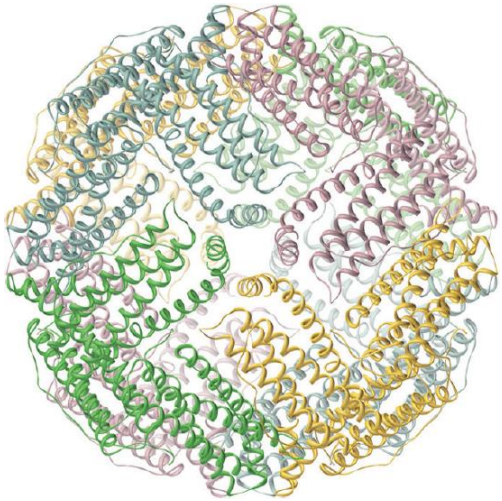


Figure 23.6.2: Ferritin, an Iron Storage Protein. A schematic drawing of the structure of iron-loaded ferritin, showing the almost spherical protein shell inside which the iron hydroxide/phosphate core is formed.

Metalloproteins and Metalloenzymes

A protein that contains one or more metal ions tightly bound to amino acid side chains is called a metalloprotein; some of the most common ligands provided by amino acids are shown here. A metalloprotein that catalyzes a chemical reaction is a metalloenzyme. Thus all metalloenzymes are metalloproteins, but the converse is not true. Recent estimates suggest that more than 40% of all known enzymes require at least one metal ion for activity, including almost all the enzymes responsible for the synthesis, duplication, and repair of DNA (deoxyribonucleic acid) and RNA (ribonucleic acid).

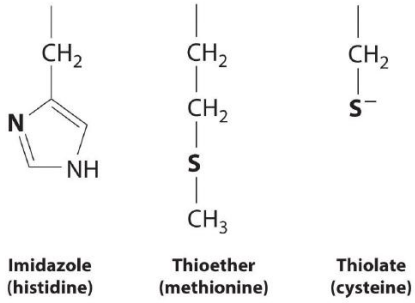


Figure 23.6.2b: Ligands used in biological systems. These metal ligands are commonly found in metalloproteins.

Electron-Transfer Proteins

Proteins whose function is to transfer electrons from one place to another are called electron-transfer proteins. Because they do not catalyze a chemical reaction, electron-transfer proteins are not enzymes; they are biochemical reductants or oxidants consumed in an enzymatic reaction. The general reaction for an electron-transfer protein is as follows:

$$M^{n+} + e^- \rightleftharpoons M^{(n-1)+} \tag{23.6.1}$$

Because many transition metals can exist in more than one oxidation state, electron-transfer proteins usually contain one or more metal ions that can undergo a redox reaction. Incorporating a metal ion into a protein has three important biological consequences:

1. The protein environment can adjust the redox potential ($E^{0\prime}$), of the metal ion over a rather large potential range, whereas the redox potential of the simple hydrated metal ion [$M_n^+(aq)$], is essentially fixed.
2. The protein can adjust the structure of the metal complex to ensure that electron transfer is rapid.
3. The protein environment provides specificity, ensuring that the electron is transferred to only the desired site.

Three important classes of metalloproteins transfer electrons: blue copper proteins, cytochromes, and iron–sulfur proteins, which generally transfer electrons at high (> 0.20 V), intermediate (±0 V), and low (−0.20 to −0.50 V) potentials, respectively (Table 23.12). Although these electron-transfer proteins contain different metals with different structures, they are all designed to ensure

rapid electron transfer to and from the metal. Thus when the protein collides with its physiological oxidant or reductant, electron transfer can occur before the two proteins diffuse apart. For electron transfer to be rapid, the metal sites in the oxidized and reduced forms of the protein must have similar structures.

Table 23.6.1: Some Properties of the Most Common Electron-Transfer Proteins

Protein	Metal Center	M/e− Transferred	Reduction Potential (V)
iron–sulfur proteins*	$[Fe(SR)_4]^{2-}$	1 Fe	−0.1 to +0.1
	$[(RS)_2FeS_2Fe(SR)_2]^{2-}$	2 Fe	−0.2 to −0.4
	$[Fe_3S_4(SR)_3]^{3-}$	3 Fe	−0.1 to −0.2
	$[Fe_4S_4(SR)_4]^{2-}$	4 Fe	−0.3 to −0.5
cytochromes	Fe-heme (low spin)	1 Fe	~0
blue copper proteins†	$[Cu(Im)_2(SR)(SR_2)]^{-}$	1 Cu	≥ +0.20

* A sulfur bound to an organic group is represented as SR.

† See Figure 23.6.2*b*: for the structure of imidazole (Im).

Blue Copper Proteins

Blue copper proteins were first isolated from bacteria in the 1950s and from plant tissues in the early 1960s. The intense blue color of these proteins is due to a strong absorption band at a wavelength of about 600 nm. Although simple Cu^{2+} complexes, such as $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$, are also blue due to an absorption band at 600 nm, the intensity of the absorption band is about 100 times less than that of a blue copper protein. Moreover, the reduction potential for the Cu^{2+}/Cu^{+} couple in a blue copper protein is usually +0.3 to +0.5 V, considerably more positive than that of the aqueous Cu^{2+}/Cu^{+} couple (+0.15 V).

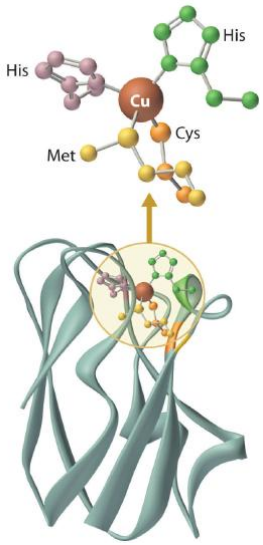


Figure 23.6.3: A Blue Copper Protein. In both the oxidized and reduced forms of a blue copper protein, the copper is coordinated by four ligands (two histidine imidazole nitrogen atoms, a cysteine thiolate sulfur, and a thioether sulfur of a methionine) in a roughly tetrahedral arrangement.

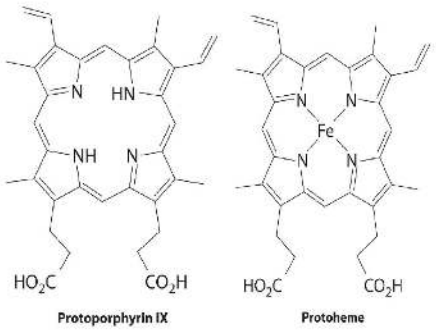
The copper center in blue copper proteins has a distorted tetrahedral structure, in which the copper is bound to four amino acid side chains (Figure 23.6.3). Although the most common structures for four-coordinate Cu^{2+} and Cu^{+} complexes are square planar and tetrahedral, respectively, the structures of the oxidized (Cu^{2+}) and reduced (Cu^{+}) forms of the protein are essentially identical. Thus the protein forces the Cu^{2+} ion to adopt a higher-energy structure that is more suitable for Cu^{+}, which makes the Cu^{2+} form easier to reduce and raises its reduction potential.

Moreover, by forcing the oxidized and reduced forms of the metal complex to have essentially the same structure, the protein ensures that electron transfer to and from the copper site is rapid because only minimal structural reorganization of the metal center is required. Kinetics studies on simple metal complexes have shown that electron-transfer reactions tend to be slow when the structures of the oxidized and reduced forms of a metal complex are very different, and fast when they are similar. You will see that other metal centers used for biological electron-transfer reactions are also set up for minimal structural reorganization after electron transfer, which ensures the rapid transfer of electrons.

Cytochromes

The cytochromes (from the Greek cytos, meaning “cell”, and chroma, meaning “color”) were first identified in the 1920s by spectroscopic studies of cell extracts. Based on the wavelength of the maximum absorption in the visible spectrum, they were classified as cytochromes a (with the longest wavelength), cytochromes b (intermediate wavelength), and cytochromes c (shortest wavelength). It quickly became apparent that there was a correlation between their spectroscopic properties and other physical properties. For examples, cytochromes c are generally small, soluble proteins with a reduction potential of about +0.25 V, whereas cytochromes b are larger, less-soluble proteins with reduction potentials of about 0 V.

All cytochromes contain iron, and the iron atom in all cytochromes is coordinated by a planar array of four nitrogen atoms provided by a cyclic tetradentate ligand called a porphyrin. The iron–porphyrin unit is called a heme group. The structures of a typical porphyrin (protoporphyrin IX) and its iron complex (protoheme) are shown here. In addition to the four nitrogen atoms of the porphyrin, the iron in a cytochrome is usually bonded to two additional ligands provided by the protein, as shown in Figure 23.6.4.



A cytochrome. Shown here is protoporphyrin IX and its iron complex, protoheme.

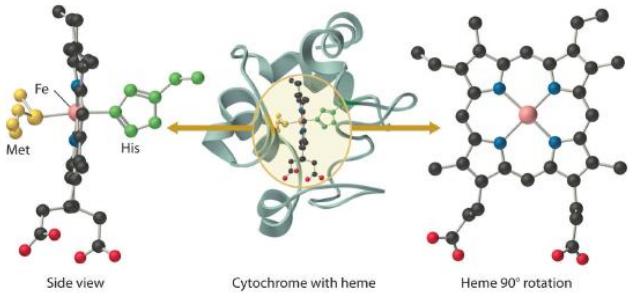


Figure 23.6.4: A Cytochrome c. In a cytochrome c, the heme iron is coordinated to the nitrogen atom of a histidine imidazole and the sulfur atom of a methionine thioether, in addition to the four nitrogen atoms provided by the porphyrin.

In contrast to the blue copper proteins, two electron configurations are possible for both the oxidized and reduced forms of a cytochrome, and this has significant structural consequences. Thus Fe^{2+} is d^6 and can be either high spin (with four unpaired electrons) or low spin (with no unpaired electrons). Similarly, Fe^{3+} is d^5 and can also be high spin (with five unpaired electrons) or low spin (with one unpaired electron). In low-spin heme complexes, both the Fe^{2+} and the Fe^{3+} ions are small enough to fit into the “hole” in the center of the porphyrin; hence the iron atom lies almost exactly in the plane of the four porphyrin nitrogen atoms in both cases. Because cytochromes b and c are low spin in both their oxidized and reduced forms, the structures of the oxidized and reduced cytochromes are essentially identical. Hence minimal structural changes occur after oxidation or reduction, which makes electron transfer to or from the heme very rapid.

> *Electron transfer reactions occur most rapidly when minimal structural changes occur during oxidation or reduction.*

Iron–Sulfur Proteins

Although all known bacteria, plants, and animals use iron–sulfur proteins to transfer electrons, the existence of these proteins was not recognized until the late 1950s. Iron–sulfur proteins transfer electrons over a wide range of reduction potentials, and their iron content can range from 1 to more than 12 Fe atoms per protein molecule. In addition, most iron–sulfur proteins contain stoichiometric amounts of sulfide (S^{2-}).

These properties are due to the presence of four different kinds of iron–sulfur units, which contain one, two, three, or four iron atoms per Fe–S complex (Figure 23.6.5). In all cases, the Fe^{2+} and Fe^{3+} ions are coordinated to four sulfur ligands in a tetrahedral environment. Due to tetrahedral coordination by weak-field sulfur ligands, the iron is high spin in both the Fe^{3+} and Fe^{2+} oxidation states, which results in similar structures for the oxidized and reduced forms of the Fe–S complexes. Consequently, only small structural changes occur after oxidation or reduction of the Fe–S center, which results in rapid electron transfer.

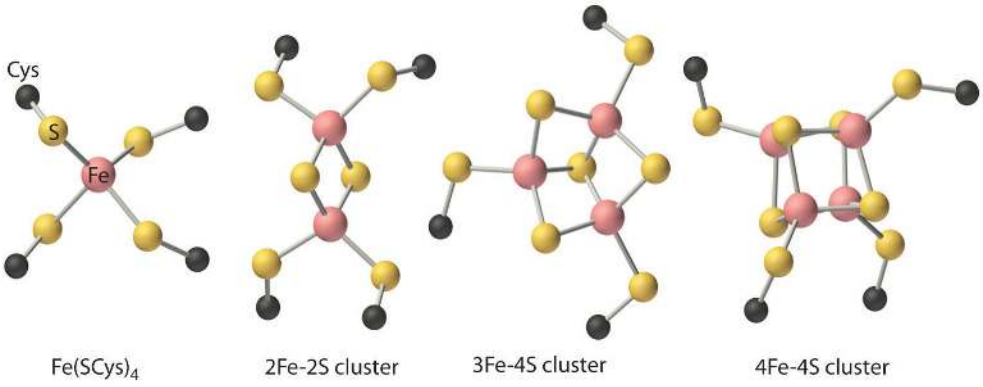


Figure 23.6.5: Fe–S Centers in Proteins: Four kinds of iron–sulfur centers, containing one, two, three, and four iron atoms, respectively, are known in electron-transfer proteins. Although they differ in the number of sulfur atoms provided by cysteine thiolates versus sulfide, in all cases the iron is coordinated to four sulfur ligands in a roughly tetrahedral environment.

Reactions of Small Molecules

Although small molecules, such as O_2, N_2, and H_2, do not react with organic compounds under ambient conditions, they do react with many transition-metal complexes. Consequently, virtually all organisms use metalloproteins to bind, transport, and catalyze the reactions of these molecules. Probably the best-known example is hemoglobin, which is used to transport O_2 in many multicellular organisms.

> *Under ambient conditions, small molecules, such as O_2, N_2, and H_2, react with transition-metal complexes but not with organic compounds.*

Oxygen Transport

Many microorganisms and most animals obtain energy by respiration, the oxidation of organic or inorganic molecules by O_2. At 25°C, however, the concentration of dissolved oxygen in water in contact with air is only about 0.25 mM. Because of their high surface area-to-volume ratio, aerobic microorganisms can obtain enough oxygen for respiration by passive diffusion of O_2 through the cell membrane. As the size of an organism increases, however, its volume increases much more rapidly than its surface area, and the need for oxygen depends on its volume. Consequently, as a multicellular organism grows larger, its need for O_2 rapidly outstrips the supply available through diffusion. Unless a transport system is available to provide an adequate supply of oxygen for the interior cells, organisms that contain more than a few cells cannot exist. In addition, O_2 is such a powerful oxidant that the oxidation reactions used to obtain metabolic energy must be carefully controlled to avoid releasing so much heat that the water in the cell boils. Consequently, in higher-level organisms, the respiratory apparatus is located in internal compartments called mitochondria, which are the power plants of a cell. Oxygen must therefore be transported not only to a cell but also to the proper compartment within a cell.

Three different chemical solutions to the problem of oxygen transport have developed independently in the course of evolution, as indicated in Table 23.6.2. Mammals, birds, reptiles, fish, and some insects use a heme protein called hemoglobin to transport oxygen from the lungs to the cells, and they use a related protein called myoglobin to temporarily store oxygen in the tissues. Several classes of invertebrates, including marine worms, use an iron-containing protein called hemerythrin to transport oxygen, whereas other classes of invertebrates (arthropods and mollusks) use a copper-containing protein called hemocyanin. Despite the presence of the hem- prefix, hemerythrin and hemocyanin do not contain a metal–porphyrin complex.

Table 23.6.2: Some Properties of the Three Classes of Oxygen-Transport Proteins

Protein	Source	M per Subunit	M per O_2 Bound	Color (deoxy form)	Color (oxy form)
hemoglobin	mammals, birds, fish, reptiles, some insects	1 Fe	1 Fe	red-purple	red
hemerythrin	marine worms	2 Fe	2 Fe	colorless	red
hemocyanin	mollusks, crustaceans, spiders	2 Cu	2 Cu	colorless	blue

Myoglobin and Hemoglobin

Myoglobin is a relatively small protein that contains 150 amino acids. The functional unit of myoglobin is an iron–porphyrin complex that is embedded in the protein (Figure 26.8.1). In myoglobin, the heme iron is five-coordinate, with only a single histidine imidazole ligand from the protein (called the proximal histidine because it is near the iron) in addition to the four nitrogen atoms of the porphyrin. A second histidine imidazole (the distal histidine because it is more distant from the iron) is located on the other side of the heme group, too far from the iron to be bonded to it. Consequently, the iron atom has a vacant coordination site, which is where O_2 binds.

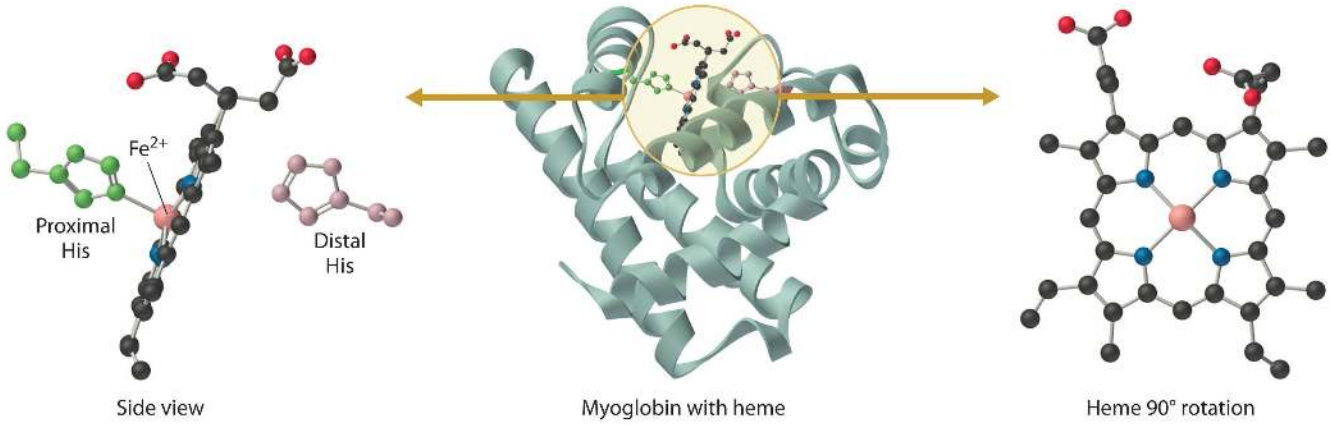


Figure 23.6.6: The Structure of Deoxymyoglobin, Showing the Heme Group. The iron in deoxymyoglobin is five-coordinate, with one histidine imidazole ligand from the protein. Oxygen binds at the vacant site on iron.

In the ferrous form (deoxymyoglobin), the iron is five-coordinate and high spin. Because high-spin Fe^{2+} is too large to fit into the "hole" in the center of the porphyrin, it is about 60 pm above the plane of the porphyrin. When O_2 binds to deoxymyoglobin to form oxymyoglobin, the iron is converted from five-coordinate (high spin) to six-coordinate (low spin; Figure 26.8.2). Because low-spin Fe^{2+} and Fe^{3+} are smaller than high-spin Fe^{2+}, the iron atom moves into the plane of the porphyrin ring to form an octahedral complex. The O_2 pressure at which half of the molecules in a solution of myoglobin are bound to O_2 ($P_{1/2}$) is about 1 mm Hg (1.3×10^{-3} atm).

> *A vacant coordination site at a metal center in a protein usually indicates that a small molecule will bind to the metal ion, whereas a coordinatively saturated metal center is usually involved in electron transfer.*

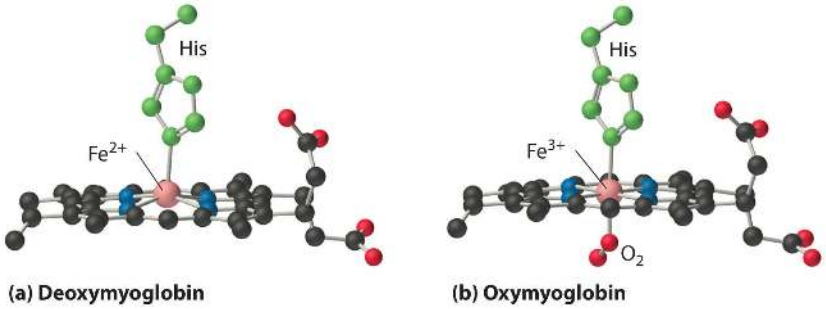


Figure 23.6.7: Oxygen Binding to Myoglobin and Hemoglobin. (a) The Fe^{2+} ion in deoxymyoglobin is high spin, which makes it too large to fit into the "hole" in the center of the porphyrin. (b) When O_2 binds to deoxymyoglobin, the iron is converted to low-spin Fe^{3+}, which is smaller, allowing the iron to move into the plane of the four nitrogen atoms of the porphyrin to form an octahedral complex.

Hemoglobin consists of two subunits of 141 amino acids and two subunits of 146 amino acids, both similar to myoglobin; it is called a tetramer because of its four subunits. Because hemoglobin has very different O_2-binding properties, however, it is not simply a "super myoglobin" that can carry four O_2 molecules simultaneously (one per heme group). The shape of the O_2-binding curve of myoglobin (Mb; Figure 23.6.7) can be described mathematically by the following equilibrium:

$$MbO_2 \rightleftharpoons Mb + O_2 \tag{23.6.2}$$

$$K_{diss} = \frac{[Mb][O_2]}{[MbO_2]} \tag{23.6.3}$$

In contrast, the O_2-binding curve of hemoglobin is S shaped (Figure 23.6.8). As shown in the curves, at low oxygen pressures, the affinity of deoxyhemoglobin for O_2 is substantially lower than that of myoglobin, whereas at high O_2 pressures the two proteins have comparable O_2 affinities. The physiological consequences of the unusual S-shaped O_2-binding curve of hemoglobin are enormous. In the lungs, where O_2 pressure is highest, the high oxygen affinity of deoxyhemoglobin allows it to be completely loaded with O_2, giving four O_2 molecules per hemoglobin. In the tissues, however, where the oxygen pressure is much lower, the decreased oxygen affinity of hemoglobin allows it to release O_2, resulting in a net transfer of oxygen to myoglobin.

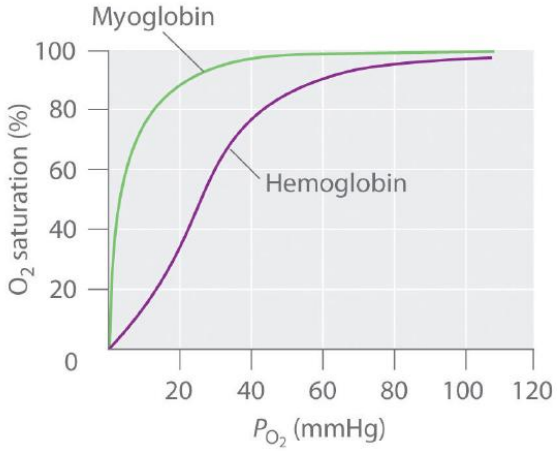


Figure 23.6.8: The O_2-Binding Curves of Myoglobin and Hemoglobin. The curve for myoglobin can be described by a simple equilibrium between deoxy- and oxymyoglobin, but the S-shaped curve for hemoglobin can be described only in terms of a cooperative interaction between the four hemes.

The S-shaped O_2-binding curve of hemoglobin is due to a phenomenon called cooperativity, in which the affinity of one heme for O_2 depends on whether the other hemes are already bound to O_2. Cooperativity in hemoglobin requires an interaction between the four heme groups in the hemoglobin tetramer, even though they are more than 3000 pm apart, and depends on the change in structure of the heme group that occurs with oxygen binding. The structures of deoxyhemoglobin and oxyhemoglobin are slightly different, and as a result, deoxyhemoglobin has a much lower O_2 affinity than myoglobin, whereas the O_2 affinity of oxyhemoglobin is essentially identical to that of oxymyoglobin. Binding of the first two O_2 molecules to deoxyhemoglobin causes

the overall structure of the protein to change to that of oxyhemoglobin; consequently, the last two heme groups have a much higher affinity for O_2 than the first two.

Oxygen is not unique in its ability to bind to a ferrous heme complex; small molecules such as CO and NO bind to deoxymyoglobin even more tightly than does O_2. The interaction of the heme iron with oxygen and other diatomic molecules involves the transfer of electron density from the filled t_{2g} orbitals of the low-spin d^6 Fe^{2+} ion to the empty π* orbitals of the ligand. In the case of the Fe^{2+}–O_2 interaction, the transfer of electron density is so great that the Fe–O_2 unit can be described as containing low-spin Fe^{3+} (d^5) and O_2^-. We can therefore represent the binding of O_2 to deoxyhemoglobin and its release as a reversible redox reaction:

$$Fe^{2+} + O_2 \rightleftharpoons Fe^{3+}{-}O_2^- \tag{23.6.4}$$

As shown in Figure 23.6.9, the Fe–O_2 unit is bent, with an Fe–O–O angle of about 130°. Because the π* orbitals in CO are empty and those in NO are singly occupied, these ligands interact more strongly with Fe^{2+} than does O_2, in which the π* orbitals of the neutral ligand are doubly occupied.

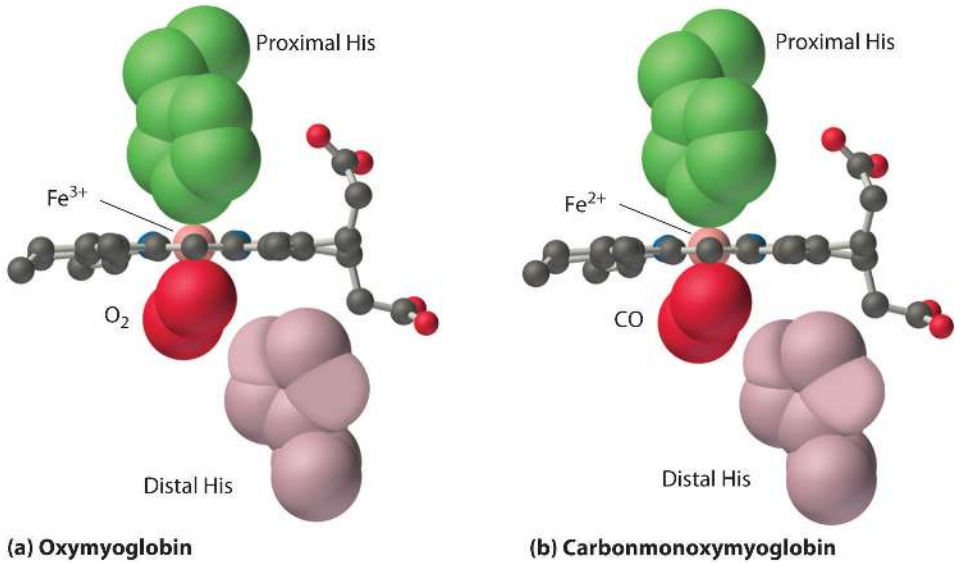


Figure 23.6.9: Binding of O_2 and CO to the Iron of Myoglobin. Because the Fe–O–O unit is bent, while the Fe–C–O unit is linear, the imidazole group of the distal histidine in hemoglobin interferes with CO binding and decreases the affinity of hemoglobin for CO.

Although CO has a much greater affinity for a ferrous heme than does O_2 (by a factor of about 25,000), the affinity of CO for deoxyhemoglobin is only about 200 times greater than that of O_2, which suggests that something in the protein is decreasing its affinity for CO by a factor of about 100. Both CO and NO bind to ferrous hemes in a linear fashion, with an Fe–C(N)–O angle of about 180°, and the difference in the preferred geometry of O_2 and CO provides a plausible explanation for the difference in affinities. As shown in Figure 23.6.9, the imidazole group of the distal histidine is located precisely where the oxygen atom of bound CO would be if the Fe–C–O unit were linear. Consequently, CO cannot bind to the heme in a linear fashion; instead, it is forced to bind in a bent mode that is similar to the preferred structure for the Fe–O_2 unit. This results in a significant decrease in the affinity of the heme for CO, while leaving the O_2 affinity unchanged, which is important because carbon monoxide is produced continuously in the body by degradation of the porphyrin ligand (even in nonsmokers). Under normal conditions, CO occupies approximately 1% of the heme sites in hemoglobin and myoglobin. If the affinity of hemoglobin and myoglobin for CO were 100 times greater (due to the absence of the distal histidine), essentially 100% of the heme sites would be occupied by CO, and no oxygen could be transported to the tissues. Severe carbon-monoxide poisoning, which is frequently fatal, has exactly the same effect. Thus the primary function of the distal histidine appears to be to decrease the CO affinity of hemoglobin and myoglobin to avoid self-poisoning by CO.

Hemerythrin

Hemerythrin is used to transport O_2 in a variety of marine invertebrates. It is an octamer (eight subunits), with each subunit containing two iron atoms and binding one molecule of O_2. Deoxyhemerythrin contains two Fe^{2+} ions per subunit and is colorless, whereas oxyhemerythrin contains two Fe^{3+} ions and is bright reddish violet. These invertebrates also contain a monomeric form of hemerythrin that is located in the tissues, analogous to myoglobin. The binding of oxygen to hemerythrin and its release can be described by the following reaction, where the HO_2^- ligand is the hydroperoxide anion derived by the deprotonation of hydrogen peroxide (H_2O_2):

$$2\,Fe^{2+} + O_2 + H^+ \rightleftharpoons 2\,Fe^{3+}{-}O_2H \tag{23.6.5}$$

Thus O_2 binding is accompanied by the transfer of two electrons (one from each Fe^{2+}) and a proton to O_2.

Hemocyanin

Hemocyanin is used for oxygen transport in many arthropods (spiders, crabs, lobsters, and centipedes) and in mollusks (shellfish, octopi, and squid); it is responsible for the bluish-green color of their blood. The protein is a polymer of subunits that each contain two copper atoms (rather than iron), with an aggregate molecular mass of greater than 1,000,000 amu. Deoxyhemocyanin contains two Cu^+ ions per subunit and is colorless, whereas oxyhemocyanin contains two Cu^{2+} ions and is bright blue. As with hemerythrin, the binding and release of O_2 correspond to a two-electron reaction:

$$2\,Cu^+ + O_2 \rightleftharpoons Cu^{2+}{-}{O_2}^{2-}{-}Cu^{2+} \tag{23.6.6}$$

Although hemocyanin and hemerythrin perform the same basic function as hemoglobin, these proteins are not interchangeable. In fact, hemocyanin is so foreign to humans that it is one of the major factors responsible for the common allergies to shellfish.

> *Myoglobin, hemoglobin, hemerythrin, and hemocyanin all use a transition-metal complex to transport oxygen.*

Enzymes Involved in Oxygen Activation

Many of the enzymes involved in the biological reactions of oxygen contain metal centers with structures that are similar to those used for O_2 transport. Many of these enzymes also contain metal centers that are used for electron transfer, which have structures similar to those of the electron-transfer proteins discussed previously. In this section, we briefly describe two of the most important examples: dioxygenases and methane monooxygenase.

Dioxygenases are enzymes that insert both atoms of O_2 into an organic molecule. In humans, dioxygenases are responsible for cross-linking collagen in connective tissue and for synthesizing complex organic molecules called prostaglandins, which trigger inflammation and immune reactions. Iron is by far the most common metal in dioxygenases; and the target of the most commonly used drug in the world, aspirin, is an iron enzyme that synthesizes a specific prostaglandin. Aspirin inhibits this enzyme by binding to the iron atom at the active site, which prevents oxygen from binding.

Methane monooxygenase catalyzes the conversion of methane to methanol. The enzyme is a monooxygenase because only one atom of O_2 is inserted into an organic molecule, while the other is reduced to water:

$$CH_4 + O_2 + 2\,e^- + 2\,H^+ \rightarrow CH_3OH + H_2O \tag{23.6.7}$$

Because methane is the major component of natural gas, there is enormous interest in using this reaction to convert methane to a liquid fuel (methanol) that is much more convenient to ship and store. Because the C–H bond in methane is one of the strongest C–H bonds known, however, an extraordinarily powerful oxidant is needed for this reaction. The active site of methane monooxygenase contains two Fe atoms that bind O_2, but the details of how the bound O_2 is converted to such a potent oxidant remain unclear.

Metal Ions as Lewis Acids

Reactions catalyzed by metal ions that do not change their oxidation states during the reaction are usually group transfer reactions, in which a group such as the phosphoryl group ($-PO_3^{2-}$) is transferred. These enzymes usually use metal ions such as Zn^{2+}, Mg^{2+}, and Mn^{2+}, and they range from true metalloenzymes, in which the metal ion is tightly bound, to metal-activated enzymes, which

require the addition of metal ions for activity. Because tight binding is usually the result of specific metal–ligand interactions, metalloenzymes tend to be rather specific for a particular metal ion. In contrast, the binding of metal ions to metal-activated enzymes is largely electrostatic in nature; consequently, several different metal ions with similar charges and sizes can often be used to give an active enzyme.

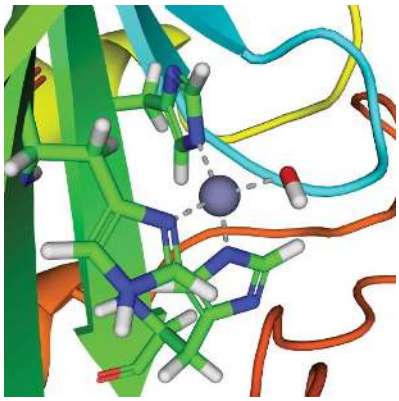
> *Metalloenzymes generally contain a specific metal ion, whereas metal-activated enzymes can use any of several metal ions of similar size and charge.*

A metal ion that acts as a Lewis acid can catalyze a group transfer reaction in many different ways, but we will focus on only one of these, using a zinc enzyme as an example. Carbonic anhydrase is found in red blood cells and catalyzes the reaction of CO_2 with water to give carbonic acid.

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{23.6.8}$$

Although this reaction occurs spontaneously in the absence of a catalyst, it is too slow to absorb all the CO_2 generated during respiration. Without a catalyst, tissues would explode due to the buildup of excess CO_2 pressure. Carbonic anhydrase contains a single Zn^{2+} ion per molecule, which is coordinated by three histidine imidazole ligands and a molecule of water. Because Zn^{2+} is a Lewis acid, the pK_a of the Zn^{2+}–OH_2 unit is about 8 versus 14 for pure water. Thus at pH 7–8, a significant fraction of the enzyme molecules contain the Zn^{2+}–OH^- group, which is much more reactive than bulk water. When carbon dioxide binds in a nonpolar site next to the Zn^{2+}–OH^- unit, it reacts rapidly to give a coordinated bicarbonate ion that dissociates from the enzyme:

$$Zn^{2+}{-}OH^- + CO_2 \rightleftharpoons Zn^{2+}{-}OCO_2H^- \rightleftharpoons Zn^{2+} + HCO_3^- \tag{23.6.9}$$



The active site of carbonic anhydrase.

Thus the function of zinc in carbonic anhydrase is to generate the hydroxide ion at pH 7.0, far less than the pH required in the absence of the metal ion.

Enzymes That Use Metals to Generate Organic Radicals

An organic radical is an organic species that contains one or more unpaired electrons. Chemists often consider organic radicals to be highly reactive species that produce undesirable reactions. For example, they have been implicated in some of the irreversible chemical changes that accompany aging. It is surprising, however, that organic radicals are also essential components of many important enzymes, almost all of which use a metal ion to generate the organic radical within the enzyme. These enzymes are involved in the synthesis of hemoglobin and DNA, among other important biological molecules, and they are the targets of pharmaceuticals for the treatment of diseases such as anemia, sickle-cell anemia, and cancer. In this section, we discuss one class of radical enzymes that use vitamin B_{12}.

Vitamin B_{12} was discovered in the 1940s as the active agent in the cure of pernicious anemia, which does not respond to increased iron in the diet. Humans need only tiny amounts of vitamin B_{12}, and the average blood concentration in a healthy adult is only about 3.5×10^{-8} M. The structure of vitamin B_{12}, shown in Figure 23.6.10, is similar to that of a heme, but it contains cobalt instead of iron, and its structure is much more complex. In fact, vitamin B_{12} has been called the most complex nonpolymeric biological

molecule known and was the first naturally occurring organometallic compound to be isolated. When vitamin B_{12} (the form present in vitamin tablets) is ingested, the axial cyanide ligand is replaced by a complex organic group.

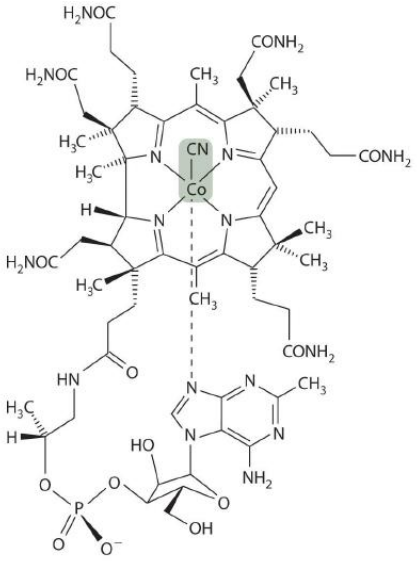
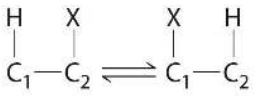


Figure 23.6.10: Vitamin B_{12} In the body, the axial cyanide ligand found in the vitamin is replaced by a complex organic unit. Heterolytic cleavage of the Co–C bond in the resulting organometallic complex generates an organic radical for the catalysis of rearrangement reactions.

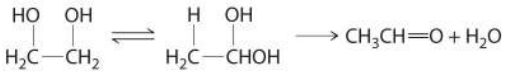
The cobalt–carbon bond in the enzyme-bound form of vitamin B_{12} and related compounds is unusually weak, and it is particularly susceptible to homolytic cleavage:

$$\mathrm{CoCH_2R} \rightleftharpoons \mathrm{Co^{2+\cdot}} + \cdot\mathrm{CH_2R} \tag{23.6.10}$$

Homolytic cleavage of the Co^{3+}–CH_2R bond produces two species, each of which has an unpaired electron: a d^7 Co^{2+} derivative and an organic radical, $\cdot CH_2R$, which is used by vitamin B_{12}-dependent enzymes to catalyze a wide variety of reactions. Virtually all vitamin B_{12}-catalyzed reactions are rearrangements in which an H atom and an adjacent substituent exchange positions:



In the conversion of ethylene glycol to acetaldehyde, the initial product is the hydrated form of acetaldehyde, which rapidly loses water:



The enzyme uses the $\cdot CH_2R$ radical to temporarily remove a hydrogen atom from the organic substrate, which then rearranges to give a new radical. Transferring the hydrogen atom back to the rearranged radical gives the product and regenerates the $\cdot CH_2R$ radical.

The metal is not involved in the actual catalytic reaction; it provides the enzyme with a convenient mechanism for generating an organic radical, which does the actual work. Many examples of similar reactions are now known that use metals other than cobalt to generate an enzyme-bound organic radical.

> *Nearly all vitamin B_{12}-catalyzed reactions are rearrangements that occur via a radical reaction.*

Summary

Three separate steps are required for organisms to obtain essential transition metals from their environment: mobilization of the metal, transport of the metal into the cell, and transfer of the metal to where it is needed within a cell or an organism. The process of iron uptake is best understood. To overcome the insolubility of $Fe(OH)_3$, many bacteria use organic ligands called siderophores, which have high affinity for Fe(III) and are secreted into the surrounding medium to increase the total concentration of dissolved iron. The iron–siderophore complex is absorbed by a cell, and the iron is released by reduction to Fe(II). Mammals use the low pH of the stomach to increase the concentration of dissolved iron. Iron is absorbed in the intestine, where it forms an Fe(III) complex with a protein called transferrin that is transferred to other cells for immediate use or storage in the form of ferritin.

Proteins that contain one or more tightly bound metal ions are called metalloproteins, and metalloproteins that catalyze biochemical reactions are called metalloenzymes. Proteins that transfer electrons from one place to another are called electron-transfer proteins. Most electron-transfer proteins are metalloproteins, such as iron–sulfur proteins, cytochromes, and blue copper proteins that accept and donate electrons. The oxidized and reduced centers in all electron-transfer proteins have similar structures to ensure that electron transfer to and from the metal occurs rapidly. Metalloproteins also use the ability of transition metals to bind small molecules, such as O_2, N_2, and H_2, to transport or catalyze the reactions of these small molecules. For example, hemoglobin, hemerythrin, and hemocyanin, which contain heme iron, nonheme iron, and copper, respectively, are used by different kinds of organisms to bind and transfer O_2. Other metalloenzymes use transition-metal ions as Lewis acids to catalyze group transfer reactions. Finally, some metalloenzymes use homolytic cleavage of the cobalt–carbon bond in derivatives of vitamin B_{12} to generate an organic radical that can abstract a hydrogen atom and thus cause molecular rearrangements to occur.

Key Takeaway

- Organisms have developed strategies to extract transition metals from the environment and use the metals in electron-transfer reactions, reactions of small molecules, Lewis-acid catalysis, and the generation of reactive organic radicals.

Conceptual Problems

1. What are the advantages of having a metal ion at the active site of an enzyme?
2. Why does the structure of the metal center in a metalloprotein that transfers electrons show so little change after oxidation or reduction?

Structure and Reactivity

1. In enzymes, explain how metal ions are particularly suitable for generating organic radicals.
2. A common method for treating carbon-monoxide poisoning is to have the patient inhale pure oxygen. Explain why this treatment is effective.

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