# INTRODUCTION TO CHEMISTRY (CHM 200)



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# Introduction to Chemistry (CHM 200)

# Title Page

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# Licensing

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# CHAPTER OVERVIEW

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# 1.1: The Scope of Chemistry

**Learning Objectives**

- To recognize the breadth, depth, and scope of chemistry.
- Define chemistry in relation to other sciences.
- Identify the main disciplines of chemistry.

Chemistry is the study of matter—what it consists of, what its properties are, and how it changes. Matter is anything that has mass and takes up space—that is, anything that is physically real. Some things are easily identified as matter—the screen on which you are reading this book, for example. Others are not so obvious. Because we move so easily through air, we sometimes forget that it, too, is matter. Because of this, chemistry is a science that has its fingers in just about everything. Being able to describe the ingredients in a cake and how they change when the cake is baked, for example, is chemistry!

Chemistry is one branch of science. Science is the process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Because the physical universe is so vast, there are many different branches of science (Figure **1.1.1**). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.

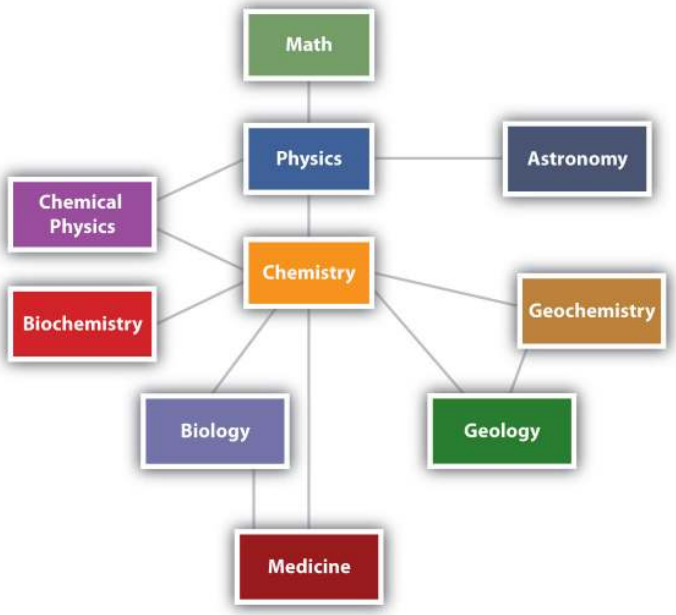



Figure **1.1.1**: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure **1.1.1** shows how many of the individual fields of science are related. At some level, all of these fields depend on matter because they all involve "stuff"; because of this, chemistry has been called the "central science", linking them all together.

> *There are many other fields of science, in addition to the ones (biology, medicine, etc.) listed here.*

### Example 1.1.1: Science Fields

Which fields of study are branches of science? Explain.

a. sculpture
b. astronomy

## Solution

a. Sculpture is not considered a science because it is not a study of some aspect of the natural universe.
b. Astronomy is the study of stars and planets, which are part of the natural universe. Astronomy is therefore a field of science.

### Exercise 1.1.1

Which fields of study are branches of science?

a. physiology (the study of the function of an animal's or a plant's body)
b. geophysics
c. agriculture
d. politics

**Answer a:**

yes

**Answer b:**

yes

**Answer c:**

yes

**Answer d:**

no

## Areas of Chemistry

The study of modern chemistry has many branches, but can generally be broken down into five main disciplines, or areas of study:

- **Physical chemistry:** Physical chemistry is the study of macroscopic properties, atomic properties, and phenomena in chemical systems. A physical chemist may study such things as the rates of chemical reactions, the energy transfers that occur in reactions, or the physical structure of materials at the molecular level.
- **Organic chemistry:** Organic chemistry is the study of chemicals containing carbon. Carbon is one of the most abundant elements on Earth and is capable of forming a tremendously vast number of chemicals (over twenty million so far). Most of the chemicals found in all living organisms are based on carbon.
- **Inorganic chemistry:** Inorganic chemistry is the study of chemicals that, in general, are not primarily based on carbon. Inorganic chemicals are commonly found in rocks and minerals. One current important area of inorganic chemistry deals with the design and properties of materials involved in energy and information technology.
- **Analytical chemistry:** Analytical chemistry is the study of the composition of matter. It focuses on separating, identifying, and quantifying chemicals in samples of matter. An analytical chemist may use complex instruments to analyze an unknown material in order to determine its various components.
- **Biochemistry:** Biochemistry is the study of chemical processes that occur in living things. Research may cover anything from basic cellular processes up to understanding disease states so that better treatments can be developed.



Figure 1.1.2: (left) Measurement of trace metals using atomic spectroscopy. (right) Measurement of hormone concentrations.

In practice, chemical research is often not limited to just one of the five major disciplines. A particular chemist may use biochemistry to isolate a particular chemical found in the human body such as hemoglobin, the oxygen carrying component of red blood cells. He or she may then proceed to analyze the hemoglobin using methods that would pertain to the areas of physical or analytical chemistry. Many chemists specialize in areas that are combinations of the main disciplines, such as bioinorganic chemistry or physical organic chemistry.

## History of Chemistry

The **history** of chemistry is an interesting and challenging one. Very early chemists were often motivated mainly by the achievement of a specific goal or product. Making perfume or soaps did not need a lot of **theory**, just a good recipe and careful attention to detail. There was no standard way of naming materials (and no periodic table that we could all agree on). It is often difficult to figure out exactly what a particular person was using. However, the science developed over the centuries by trial and error.

Major progress was made toward putting chemistry on a solid foundation when Robert Boyle (1637-1691) began his **research** in chemistry (Figure 1.1.3). He developed the basic ideas about the behavior of gases. He could then describe gases mathematically. Boyle also helped form the idea that small particles could combine to form molecules. Many years later, John Dalton used these ideas to develop the atomic theory.



Figure 1.1.3: Robert Boyle.

The field of chemistry began to develop rapidly in the 1700's. Joseph Priestley (1733-1804) isolated and characterized several gases: oxygen, carbon monoxide, and nitrous oxide. It was later discovered that nitrous oxide ("laughing gas") worked as an anesthetic. This gas was used for that purpose for the first time in 1844 during a tooth extraction. Other gases discovered during that time were chlorine, by C.W. Scheele (1742-1786) and nitrogen, by Antoine Lavoisier (1743-1794). Lavoisier has been considered by many scholars to be the "father of chemistry". Among other accomplishments, he discovered the role of oxygen in combustion and definitively formulated the law of conservation of matter.

Chemists continued to discover new compounds in the 1800's. The science also began to develop a more theoretical foundation. John Dalton (1766-1844) put forth his atomic theory in 1807. This idea allowed scientists to think about chemistry in a much more systematic way. Amadeo Avogadro (1776-1856) laid the groundwork for a more quantitative approach to chemistry by calculating the number of particles in a given amount of a gas. A lot of effort was put forth in studying chemical reactions. These efforts led to new materials being produced. Following the invention of the battery by Alessandro Volta (1745-1827), the field of electrochemistry (both theoretical and applications) developed through major contributions by Humphry Davy (1778-1829) and Michael Faraday (1791-1867). Other areas of the discipline also progressed rapidly.

It would take a large book to cover developments in chemistry during the twentieth century and up to today. One major area of expansion was in the area of the chemistry of living processes. Research in photosynthesis in plants, the discovery and

characterization of enzymes as biochemical catalysts, elucidation of the structures of biomolecules such as insulin and DNA—these efforts gave rise to an explosion of information in the field of biochemistry.

The practical aspects of chemistry were not ignored. The work of Volta, Davy, and Faraday eventually led to the development of batteries that provided a source of electricity to power a number of devices (Figure **1.1.4**).

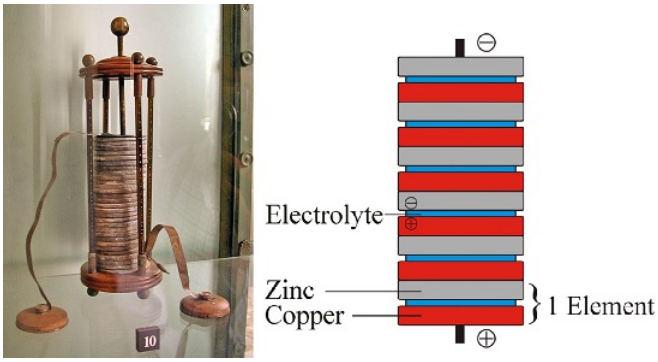



Figure **1.1.4**: Battery developed by Volta. (CC BY-SA 3.0; (left) GuidoB and (right) Kkkdc).

Charles Goodyear (1800-1860) discovered the process of vulcanization, allowing a stable rubber product to be produced for the tires of all the vehicles we have today. Louis Pasteur (1822-1895) pioneered the use of heat sterilization to eliminate unwanted microorganisms in wine and milk. Alfred Nobel (1833-1896) invented dynamite (Figure **1.1.5**). After his death, the fortune he made from this product was used to fund the Nobel Prizes in science and the humanities. J.W. Hyatt (1837-1920) developed the first plastic. Leo Baekeland (1863-1944) developed the first synthetic resin, widely used for inexpensive and sturdy dinnerware.



Figure **1.1.5**: Dynamite explosion in Panama, Central America (1908).

Today, chemistry continues to be essential to the development of new materials and technologies, from semiconductors for electronics to powerful new medicines, and beyond.

## Summary

- Chemistry is the study of matter and the changes it undergoes and considers both *macroscopic* and *microscopic* information.
- Matter is anything that has mass and occupies space.
- The five main disciplines of chemistry are physical chemistry, organic chemistry, inorganic chemistry, analytical chemistry and biochemistry.
- Many civilizations contributed to the growth of chemistry. A lot of early chemical research focused on practical uses. Basic chemistry theories were developed during the nineteenth century. New materials and batteries are a few of the products of modern chemistry.

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# 1.2: What is Matter?

**Learning Objectives**

- Define matter and explain how it is composed of building blocks known as "atoms".

We are all familiar with matter. The definition of **Matter** is anything that has mass and volume (takes up space). For most common objects that we deal with every day, it is fairly simple to demonstrate that they have mass and take up space. You might be able to imagine, however, the difficulty for people several hundred years ago to demonstrate that air had mass and volume. Air (and all other gases) are invisible to the eye, have very small masses compared to equal amounts of solids and liquids, and are quite easy to compress (change volume). Without sensitive equipment, it would have been difficult to convince people that gases are matter. Today, we can measure the mass of a small balloon when it is deflated and then blow it up, tie it off, and measure its mass again to detect the additional mass due to the air inside. The mass of air, under room conditions, that occupies a one quart jar is approximately 0.0002 pounds. This small amount of mass would have been difficult to measure in times before balances were designed to accurately measure very small masses. Later, scientists were able to compress gases into such a small volume that the gases turned into liquids, which made it clear that gases are matter.



Figure **1.2.1**: Everything from an ant, to a truck, to the earth, and even the entire galaxy is composed of matter. Images used with permission from Wikipedia (CC_SA-BY-3.0; credit High Contrast).

Even though the universe consists of "things" as wildly different as ants and galaxies, the matter that makes up all of these "things" is composed of a very limited number of building blocks. These building blocks are known as **atoms**, and so far, scientists have discovered or created a grand total of 118 different types of atoms. Scientists have given a name to each different type of atom. A substance that is composed of only one type of atom is called an element. At this point, what should amaze you is that all forms of matter in our universe are made with only 118 different building blocks. In some ways, it's sort of like cooking a gourmet, five-course meal using only three ingredients! How is it possible? To answer that question, you have to understand the ways in which different elements are put together to form matter.

The most important method that nature uses to organize atoms into matter is the formation of **molecules**. Molecules are groups of two or more atoms that have been bonded together. There are millions of different ways to bond atoms together, which means that

there are millions of different possible molecules. Each of these molecules has its own set of chemical properties, and it's these properties with which chemists are most concerned. You will learn a lot more about atoms and molecules, including how they were discovered, in a later part of the textbook.

## Summary

All matter has mass and occupies space. All physical objects are made of matter. Matter itself is composed of tiny building blocks known as "atoms". There are only 118 different types of atoms known to man. Frequently, atoms are bonded together to form "molecules".

## Contributions & Attributions

- Wikipedia

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# 1.2.1: Classifying Matter According to Its State—Solid, Liquid, and Gas

**Learning Objectives**

- To describe the solid, liquid and gas phases.

Water can take many forms. At low temperatures (below **0°C**), it is a solid. When at "normal" temperatures (between **0°C** and **100°C**), it is a liquid. While at temperatures above **100°C**, water is a gas (steam). The state that water is in depends upon the temperature. Each state has its own unique set of physical properties. Matter typically exists in one of three states: **solid**, **liquid**, or **gas**.

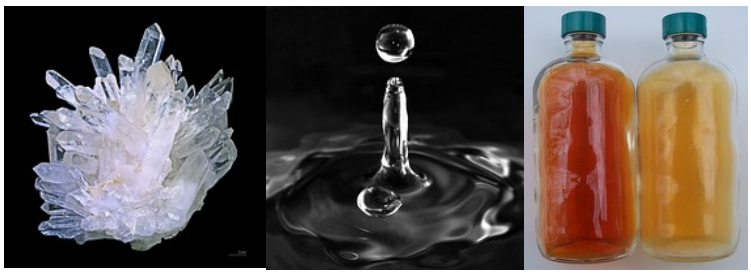


Figure **1.2.1.1**: Matter is usually classified into three classical states, with plasma sometimes added as a fourth state. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

The state that a given substance exhibits is also a physical property. Some substances exist as gases at room temperature (oxygen and carbon dioxide), while others, like water and mercury metal, exist as liquids. Most metals exist as solids at room temperature. All substances can exist in any of these three states. Figure **1.2.1.2** shows the differences among solids, liquids, and gases at the molecular level. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

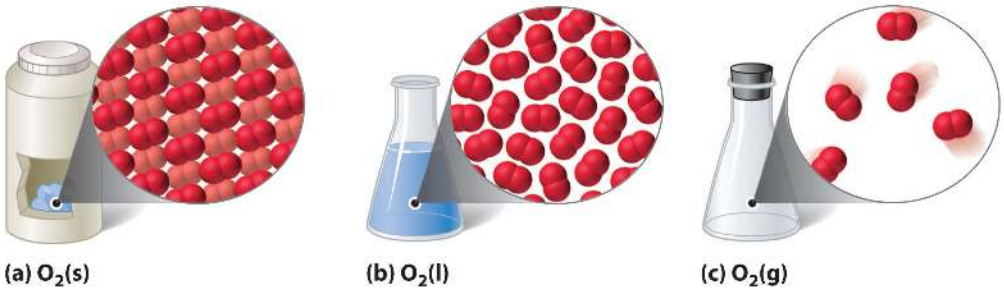
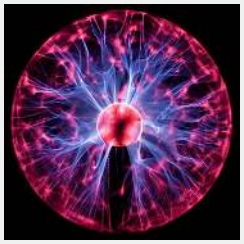



Figure **1.2.1.2**: A Representation of the Solid, Liquid, and Gas States. (a) Solid $O_2$ has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid $O_2$ conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous $O_2$ fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

**Plasma: A Fourth State of Matter**

Technically speaking, a fourth state of matter called plasma exists, but it does not naturally occur on earth, so we will omit it from our study here.



A plasma globe operating in a darkened room. (CC BY-SA 3.0; Chocolateoak).

## Solids

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle.

Solids are defined by the following characteristics:

- Definite shape (rigid)
- Definite volume
- Particles vibrate around fixed axes

If we were to cool liquid mercury to its freezing point of $-39°C$, and under the right pressure conditions, we would notice all of the liquid particles would go into the solid state. Mercury can be solidified when its temperature is brought to its freezing point. However, when returned to room temperature conditions, mercury does not exist in solid state for long, and returns back to its more common liquid form.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a **crystal**. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure 1.2.1.3. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, "without form") solids. Glass is one example of an amorphous solid.

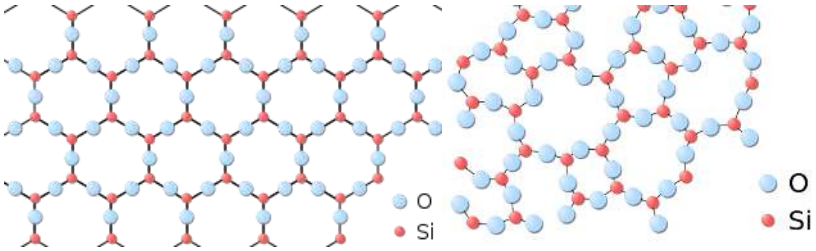



Figure 1.2.1.3: (left) The periodic crystalline lattice structure of quartz $SiO_2$ in two-dimensions. (right) The random network structure of glassy $SiO_2$ in two-dimensions. Note that, as in the crystal, each Silicon atom is bonded to 4 oxygen atoms, where the fourth oxygen atom is obscured from view in this plane. Images used with permission (public domain).

## Liquids

If the particles of a substance have enough energy to partially overcome intermolecular interactions, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and takes a shape dictated by its container.

Liquids have the following characteristics:

- No definite shape (takes the shape of its container).
- Has definite volume.
- Particles are free to move over each other, but are still attracted to each other.

A familiar liquid is mercury metal. Mercury is an anomaly. It is the only metal we know of that is liquid at room temperature. Mercury also has an ability to stick to itself (surface tension)—a property that all liquids exhibit. Mercury has a relatively high surface tension, which makes it very unique. Here you see mercury in its common liquid form.



***Video* 1.2.1.1***: Mercury boiling to become a gas.*

If we heat liquid mercury to its boiling point of $357^{\circ}C$ under the right pressure conditions, we would notice all particles in the liquid state go into the gas state.

## Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. This describes the gas state, which we will consider in more detail elsewhere. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either. The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Gases have the following characteristics:

- No definite shape (takes the shape of its container)
- No definite volume
- Particles move in random motion with little or no attraction to each other
- Highly compressible

Table 1.2.1.1: Characteristics of the Three States of Matter

| Characteristics | Solids | Liquids | Gases |
|---|---|---|---|
| shape | definite | indefinite | indefinite |
| volume | definite | definite | indefinite |
| relative intermolecular interaction strength | strong | moderate | weak |
| relative particle positions | in contact and fixed in place | in contact but not fixed | not in contact, random positions |

### Example 1.2.1.1

What state or states of matter does each statement, describe?

a. This state has a definite volume, but no definite shape.
b. This state has no definite volume.
c. This state allows the individual particles to move about while remaining in contact.

#### Solution

a. This statement describes the liquid state.
b. This statement describes the gas state.
c. This statement describes the liquid state.

## Exercise 1.2.1.1

What state or states of matter does each statement describe?

a. This state has individual particles in a fixed position with regard to each other.
b. This state has individual particles far apart from each other in space.
c. This state has a definite shape.

**Answer a:**

solid

**Answer b:**

gas

**Answer c:**

solid

## Summary

- Three states of matter exist—solid, liquid, and gas.
- Solids have a definite shape and volume.
- Liquids have a definite volume, but take the shape of the container.
- Gases have no definite shape or volume.

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# 1.2.2: Classification of Matter

**Learning Objectives**

- Categorize different types of matter as a pure substances or mixtures.
- Explain the difference between an element and a compound.
- Explain the difference between a homogeneous mixture and a heterogeneous mixture.

One useful way of organizing our understanding of matter is to think of a hierarchy that extends down from the most general and complex substances to the simplest and most fundamental (Figure **1.2.2.1**). At the top of this hierarchy is two broad categories into which all matter can be classified: pure substances and mixtures. A **pure substance** is a form of matter that has a constant composition (meaning that all samples of this substance have uniform composition) and properties that are constant throughout the sample (meaning that there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). If we take two or more pure substances and physically mix them together, we refer to this as a **mixture**. A mixture does not have constant composition or properties throughout.

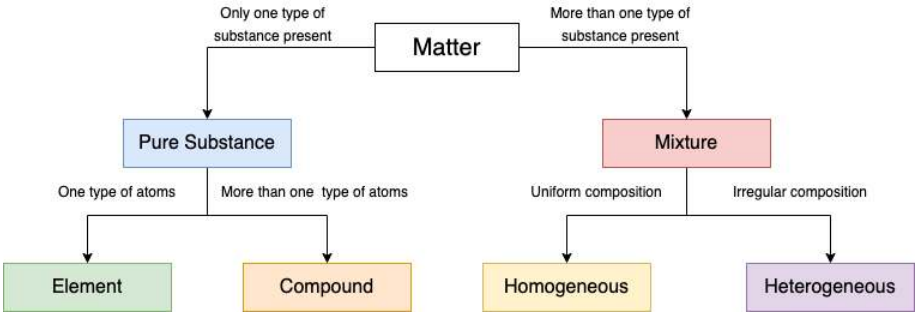



Figure **1.2.2.1**: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.

Elements and compounds are both examples of pure substances. A substance that cannot be broken down into chemically simpler components is an **element**. Oxygen, O, and hydrogen, H, are each examples of elements. A pure substance that can be broken down into chemically simpler components (because it made up of more than one element) is a **compound**. For example, the compound water, $H_2O$, is formed when hydrogen and oxygen chemically combine in a fixed ratio of 2 hydrogen atoms for every 1 oxygen atom.

Compounds may have different chemical and physical properties from the individual elements that they are composed of. Mixtures, on the other hand, are physical blends of two or more components, each of which retains its own identity and properties. Mixtures can always be separated again into the component pure substances, because bonding among the atoms of the constituent substances does not occur. For example sodium is a soft shiny metal and chlorine is a pungent green gas. These two elements chemically combine to form the *compound*, sodium chloride (table salt) which is a white, crystalline solid having *none* of the properties of either sodium or chlorine. If, however, you *mixed* table salt with ground pepper, you would still be able to see the individual grains of each of them and, if you were patient, you could take tweezers and carefully separate them back into pure salt and pure pepper.

Mixtures fall into two categories, based on the uniformity of their composition (Figure **1.2.2.1**). The first, called a **heterogeneous mixture**, is distinguished by the fact that different samples of the mixture may have a different composition. For example, if you open a container of mixed nuts and pull out a series of small samples and examine them, the exact ratio of peanuts-to-almonds in the samples will always be slightly different, no matter how carefully you mix them. Common examples of heterogeneous mixtures include dirt, gravel, and vegetable soup.

In a **homogeneous mixture,** on the other hand, any sample that you examine will have exactly the *same* composition as any other sample. Within chemistry, the most common type of homogeneous mixture is a **solution** which is one substance dissolved completely within another. Think of a solution of pure sugar dissolved in pure water. Any sample of the solution that you examine will have *exactly* the same ratio of sugar-to-water, which means that it is a homogeneous mixture. Even in a homogeneous mixture, the properties of the components are generally recognizable. Thus, sugar-water tastes sweet (like sugar) and is wet (like water). Unlike a compound, which has a fixed, definite ratio, in a mixture the amounts of each component can vary. For example, when

you add a little sugar to one cup of tea and a lot of sugar to another, each cup will contain a homogeneous mixture of tea and sugar but they will have a different ratio of sugar-to-tea and a different taste. If you add so much sugar that some does not dissolve and stays on the bottom, however, the mixture is no longer homogeneous, it is heterogeneous; you could easily separate the two components (Figure 1.2.2.1).

### Example 1.2.2.1

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:

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

### Exercise 1.2.2.1

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:**

homogeneous mixture (solution)

**Answer b:**

element

**Answer c:**

heterogeneous mixture

**Answer d:**

compound

### Example 1.2.2.2

How would a chemist categorize each example of matter?

a. saltwater
b. soil
c. water
d. oxygen

**Solution**

a. Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a homogeneous mixture, or a solution.
b. Soil is composed of small pieces of a variety of different materials, so it is a heterogeneous mixture.
c. Water is a substance; more specifically, because water is composed of a fixed ratio hydrogen and oxygen atoms, it is a compound.
d. Oxygen, a substance, is an element.

### Exercise 1.2.2.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

**Answer a:**

Coffee, assuming it is filtered, is a variety of substances dissolved in water, therefore, it is a homogeneous mixture, or a solution.

**Answer b:**

Hydrogen is a known element.

**Answer c:**

An egg is composed of many different substances with different compositions between the yolk and white, it is a heterogeneous mixture.

## Summary

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample. Mixtures are physical combinations of two or more elements and/or compounds. Mixtures can be classified as homogeneous or heterogeneous. Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

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# 1.2.3: Differences in Matter- Physical and Chemical Properties

**Learning Objectives**

- Define chemical and physical properties.
- Identify chemical and physical properties.

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

## Physical Property

A *physical property* is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Silver is a shiny metal that conducts electricity very well. It can be molded into thin sheets, a property called malleability. Salt is dull and brittle and conducts electricity when it has been dissolved into water, which it does quite easily. Physical properties of matter include color, hardness, malleability, solubility, electrical conductivity, density, melting point, and boiling point.

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red. However, density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum. Pure water, for example, has a density of 0.998 $g/cm^3$ at 25°C. The average densities of some common substances are in Table **1.2.3.1**. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table **1.2.3.1**: Densities of Common Substances

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

Hardness helps determine how an element (especially a metal) might be used. Many elements are fairly soft (silver and gold, for example) while others (such as titanium, tungsten, and chromium) are much harder. Carbon is an interesting example of hardness. In graphite, (the "lead" found in pencils) the carbon is very soft, while the carbon in a diamond is roughly seven times as hard.



Figure 1.2.3.1: Pencil (left) and Diamond ring (right). Both are a form of carbon, but exhibit very different physical properties.

Melting and boiling points are somewhat unique identifiers, especially of compounds. In addition to giving some idea as to the identity of the compound, important information can be obtained about the purity of the material.

## Chemical Properties

**Chemical properties** of matter describe its potential to undergo some chemical change or reaction by virtue of its composition. The elements, electrons, and bonds that are present give the matter potential for chemical change. It is quite difficult to define a chemical property without using the word "change". Eventually, after studying chemistry for some time, you should be able to look at the formula of a compound and state some chemical property. For example, hydrogen has the potential to ignite and explode given the right conditions—this is a chemical property. Metals in general have the chemical property of reacting with an acid. Zinc reacts with hydrochloric acid to produce hydrogen gas—this is a chemical property.



Figure 1.2.3.2: Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. (CC BY-SA 3.0; Marlith).

A chemical property of iron is its capability of combining with oxygen to form iron oxide, the chemical name of rust (Figure 1.2.3.2). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Table 1.2.3.2: Contrasting Physical and Chemical Properties

| Physical Properties | Chemical Properties |
|---|---|
| Gallium metal melts at 30 $^{o}$C. | Iron metal rusts. |
| Mercury is a very dense liquid. | A green banana turns yellow when it ripens. |
| Gold is shiny. | A dry piece of paper burns. |

### Example 1.2.3.1

Which of the following is a chemical property of iron?

a. Iron corrodes in moist air.
b. Density = 7.874 g/cm$^3$
c. Iron is soft when pure.
d. Iron melts at 1808 K.

#### Solution

"Iron corrodes in moist air" is the only chemical property of iron from the list.

### Exercise 1.2.3.1A

Which of the following is a physical property of matter?

a. corrosiveness
b. pH (acidity)
c. density
d. flammability

**Answer**

c

### Exercise 1.2.3.1B

Which of the following is a chemical property?

a. flammability
b. melting point
c. boiling point
d. density

**Answer**

a

## Summary

A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Physical properties include color, density, hardness, and melting and boiling points. A chemical property describes the ability of a substance to undergo a specific chemical change. To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed.

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# 1.2.4: Changes in Matter - Physical and Chemical Changes

**Learning Objectives**

- Label a change as chemical or physical.
- List evidence that can indicate a chemical change occurred.

Change is happening all around us all of the time. Just as chemists have classified elements and compounds, they have also classified types of changes. Changes are classified as either physical or chemical changes. Chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.

## Physical Change

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

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

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. Melting is an example of a physical change. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. When liquid water is heated, it changes to water vapor. However, even though the physical properties have changed, the molecules are exactly the same as before. We still have each water molecule containing two hydrogen atoms and one oxygen atom covalently bonded. When you have a jar containing a mixture of pennies and nickels and you sort the mixture so that you have one pile of pennies and another pile of nickels, you have not altered the identity of the pennies or the nickels—you've merely separated them into two groups. This would be an example of a physical change. Similarly, if you have a piece of paper, you don't change it into something other than a piece of paper by ripping it up. What was paper before you started tearing is still paper when you are done. Again, this is an example of a physical change.



Figure 1.2.4.1: Ice melting is a physical change. When liquid water ($H_2O$) freezes into a solid state (ice), it appears changed; however, this change is only physical, as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (Public Domain; Moussa).

Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.

## Chemical Change

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

One good example of a chemical change is burning a candle. The act of burning paper actually results in the formation of new chemicals (carbon dioxide and water) from the burning of the wax. Another example of a chemical change is what occurs when natural gas is burned in your furnace. This time, on the left there is a molecule of methane, $\mathrm{CH_4}$, and two molecules of oxygen, $\mathrm{O_2}$; on the right are two molecules of water, $\mathrm{H_2O}$, and one molecule of carbon dioxide, $\mathrm{CO_2}$. In this case, not only has the appearance changed, but the structure of the molecules has also changed. The new substances do not have the same chemical properties as the original ones. Therefore, this is a chemical change.



Figure 1.2.4.2: Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos )

We can't actually see molecules breaking and forming bonds, although that's what defines chemical changes. We have to make other observations to indicate that a chemical change has happened. Some of the evidence for chemical change will involve the energy changes that occur in chemical changes, but some evidence involves the fact that new substances with different properties are formed in a chemical change.

Observations that help to indicate chemical change include:

- Temperature changes (either the temperature increases or decreases).
- Light given off.
- Unexpected color changes (a substance with a different color is made, rather than just mixing the original colors together).
- Bubbles are formed (but the substance is not boiling—you made a substance that is a gas at the temperature of the beginning materials, instead of a liquid).
- Different smell or taste (do not taste your chemistry experiments, though!).
- A solid forms if two clear liquids are mixed (look for *floaties*—technically called a precipitate).

### Example 1.2.4.1

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

a. Boiling water.
b. A nail rusting.
c. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
d. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

#### Solution

a. Physical: boiling and melting are physical changes. When water boils, no bonds are broken or formed. The change could be written: $\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$

b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $Fe + O_2 \rightarrow Fe_2O_3$
c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.
d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

**? Exercise 1.2.4.1**

Label each of the following changes as a physical or chemical change.

a. A mirror is broken.
b. An iron nail corroded in moist air
c. Copper metal is melted.
d. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

**Answer a:**

physical change

**Answer b:**

chemical change

**Answer c:**

physical change

**Answer d:**

chemical change

## Separating Mixtures Through Physical Changes

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

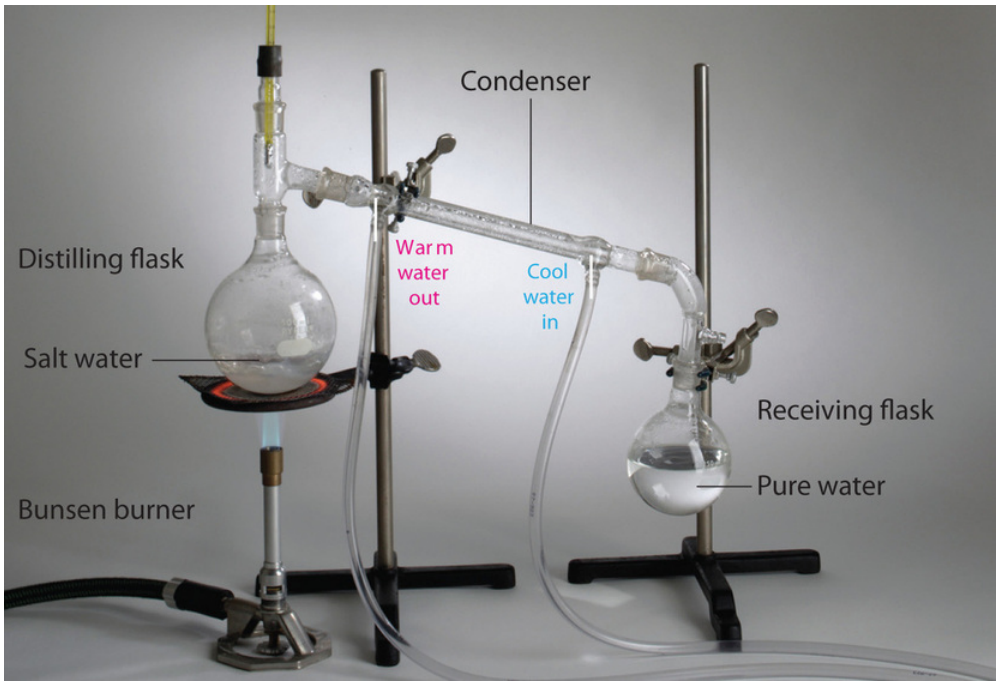



Figure **1.2.4.3:** *The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.*

Parts of a distillation setup: Bunsen burner, salt water in distilling flask, condenser with cool water in and warm water out, pure water in receiving flask

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

Another example for using physical properties to separate mixtures is filtration (Figure **1.2.4.4**). Filtration is any mechanical, physical or biological operation that separates solids from fluids (liquids or gases) by adding a medium through which only the fluid can pass. The fluid that passes through is called the filtrate. There are many different methods of filtration; all aim to attain the separation of substances. Separation is achieved by some form of interaction between the substance or objects to be removed and the filter. The substance that is to pass through the filter must be a fluid, i.e. a liquid or gas. Methods of filtration vary depending on the location of the targeted material, i.e. whether it is dissolved in the fluid phase or suspended as a solid.

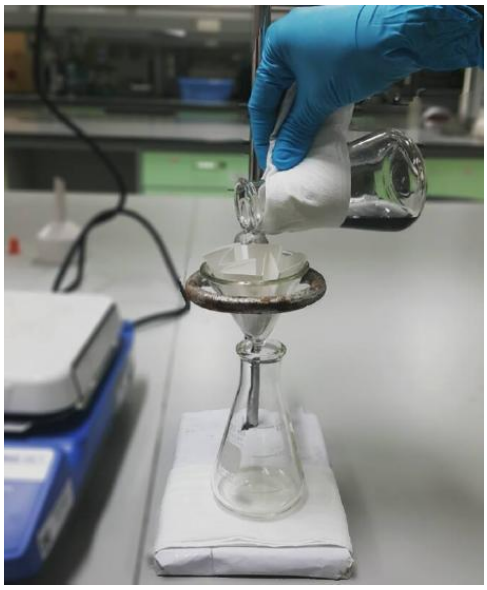


Figure **1.2.4.4***: Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

## Summary

- Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.
- Physical changes are changes that do not alter the identity of a substance.
- Chemical changes are changes that occur when one substance is turned into another substance.
- Chemical changes are frequently harder to reverse than physical changes. Observations that indicate a chemical change has occurred include color change, temperature change, light given off, formation of bubbles, formation of a precipitate, etc.

## Contributions & Attributions

- 
- Boundless (www.boundless.com)

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# 1.3: Physical Quantities- Units and Scientific Notation

**Learning Objectives**

- Express quantities properly using a number and a unit.
- Recognize the different measurement systems used in chemistry.
- Describe how prefixes are used in the metric system and identify how the prefixes milli-, centi-, and kilo- compare to the base unit.
- Understand when and how to use scientific notation to represent measurements.

## Measurements

A coffee maker's instructions tell you to fill the coffeepot with 4 cups of water and use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor's office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure **1.3.1**); the nurse is also measuring.



Figure **1.3.1**: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. (GNU Free Documentation License; Pia von Lützau via Wikipedia).

Chemists measure the properties of matter using a variety of devices or measuring tools, many of which are similar to those used in everyday life. Rulers are used to measure length, balances (scales) are used to measure mass (weight), and graduated cylinders or pipettes are used to measure volume. Measurements made using these devices are expressed as quantities. A quantity is an amount of something and consists of a **number** and a **unit**. The number tells us *how many* (or how much), and the unit tells us what the scale of measurement is. For example, when a distance is reported as "5.2 kilometers," we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5.2.

$$\underbrace{5.2}_{\text{number}}\ \underbrace{\text{kilometers}}_{\text{unit}}$$

If you ask a friend how far he or she walks from home to school, and the friend answers "12" without specifying a unit, you do not know whether your friend walks—for example, 12 miles, 12 kilometers, 12 furlongs, or 12 yards.

Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

> *Both a number and a unit must be included to express a quantity properly.*

To understand chemistry, we need a clear understanding of the units chemists work with and the rules they follow for expressing numbers.

**Example 1.3.1**

Identify the ***number*** and the ***unit*** in each quantity.

a. one dozen eggs
b. 2.54 centimeters
c. a box of pencils
d. 88 meters per second

**Answers**

a. The number is one, and the unit is dozen.
b. The number is 2.54, and the unit is centimeter.
c. The number 1 is implied because the quantity is only a box. The unit is box of pencils.
d. The number is 88, and the unit is meters per second. Note that in this case the unit is actually a combination of two units: meters and seconds.

**Exercise 1.3.2**

Identify the ***number*** and the ***unit*** in each quantity.

a. 99 bottles of soda
b. 60 miles per hour
c. 32 fluid ounces
d. 98.6 degrees Fahrenheit

**Answer a**

The number is 99, and the unit is bottles of soda.

**Answer b**

The number is 60, and the unit is miles per hour.

**Answer c**

The number 32, and the unit is fluid ounces

**Answer d**

The number is 98.6, and the unit is degrees Fahrenheit

## The International System of Units

How long is a yard? It depends on whom you ask and when you asked the question. Today we have a standard definition of the yard, which you can see marked on every football field. If you move the ball ten yards, you get a first down and it doesn't matter whether you are playing in Los Angeles, Dallas, or Green Bay. But at one time that yard was arbitrarily defined as the distance from the tip of the king's nose to the end of his outstretched hand. Of course, the problem there is simple: new king, new distance (and then you have to remark all those football fields).

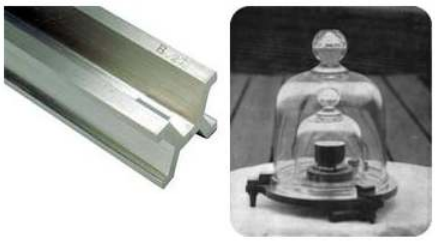


Figure **1.3.2**: Meter standard (left) and Kilogram standard (right).

## SI Base Units

All measurements depend on the use of units that are well known and understood. The **English system** of measurement units (inches, feet, ounces, etc.) are not used in science because of the difficulty in converting from one unit to another. The **metric system** is used because all metric units are based on multiples of 10, making conversions very simple. The metric system was originally established in France in 1795. **The International System of Units** is a system of measurement based on the metric system. The acronym **SI** is commonly used to refer to this system and stands for the French term, *Le Système International d'Unités*. The SI was adopted by international agreement in 1960 and is composed of seven base units in Table **1.3.1**.

Table **1.3.1**: SI Base Units of Measurement

| Quantity | SI Base Unit | Symbol |
|---|---|---|
| Length | meter | **m** |
| Mass | kilogram | **kg** |
| Temperature | kelvin | **K** |
| Time | second | **s** |
| Amount of a Substance | mole | **mol** |
| Electric Current | ampere | **A** |
| Luminous Intensity | candela | **cd** |

The first units are frequently encountered in chemistry. All other measurement quantities, such as volume, force, and energy, can be derived from these seven base units.

### The Metric System is Not Ubiquitously Adopted

The map below shows the adoption of the SI units in countries around the world. The United States has legally adopted the metric system for measurements, but does not use it in everyday practice. Great Britain and much of Canada use a combination of metric and imperial units.

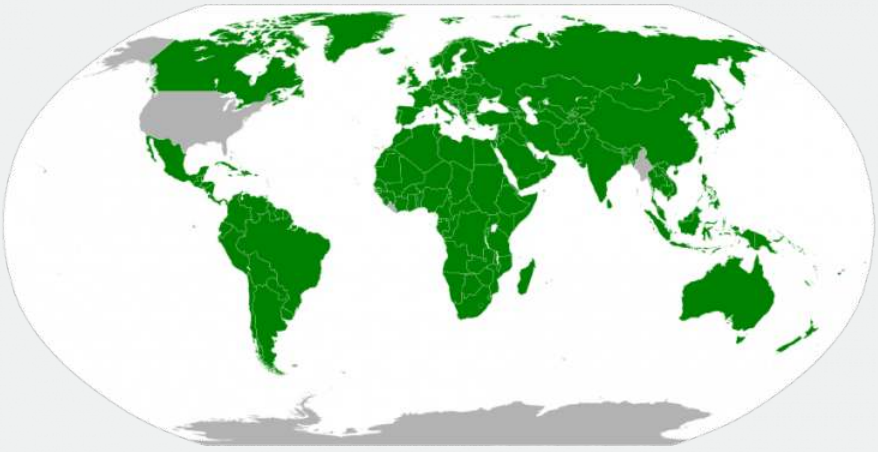


Figure **1.3.2**: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

## Metric Prefixes

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size. These prefixes all derive from either Latin or Greek terms.

For example, *mega* comes from the Greek word μεγας, meaning "great". Table **1.3.2** lists the most common metric prefixes and their relationship to the central unit that has no prefix. Length is used as an example to demonstrate the relative size of each prefixed unit.

Table **1.3.2**: SI Prefixes. Commonly used prefixes are bolded.

| Prefix | Unit Abbreviation | Meaning | Example |
|---|---|---|---|
| giga | **G** | 1,000,000,000 | 1 gigameter $(\mathbf{Gm}) = 10^9\ \mathbf{m}$ |
| mega | **M** | 1,000,000 | 1 megameter $(\mathbf{Mm}) = 10^6\ \mathbf{m}$ |
| **kilo** | **k** | **1,000** | **1 kilo**meter $(\mathbf{km}) = 1,000\ \mathbf{m}$ |
| hecto | **h** | 100 | 1 hectometer $(\mathbf{hm}) = 100\ \mathbf{m}$ |
| deka | **da** | 10 | 1 dekameter $(\mathbf{dam}) = 10\ \mathbf{m}$ |
| | | **1** | 1 meter $(\mathbf{m})$ |
| **deci** | **d** | **1/10** | **1 deci**meter $(\mathbf{dm}) = 0.1\ \mathbf{m}$ |
| **centi** | **c** | **1/100** | **1 centi**meter $(\mathbf{cm}) = 0.01\ \mathbf{m}$ |
| **milli** | **m** | **1/1,000** | **1 milli**meter $(\mathbf{mm}) = 0.001\ \mathbf{m}$ |
| **micro** | **μ** | **1/1,000,000** | **1 micro**meter $(\mu\mathbf{m}) = 10^{-6}\ \mathbf{m}$ |
| nano | **n** | 1/1,000,000,000 | 1 nanometer $(\mathbf{nm}) = 10^{-9}\ \mathbf{m}$ |
| pico | **p** | 1/1,000,000,000,000 | 1 picometer $(\mathbf{pm}) = 10^{-12}\ \mathbf{m}$ |

Just as expressing a quantity without a unit is meaningless, so is using the incorrect format for units and prefixes. As you may have noticed, most metric abbreviations are lowercase. We use "**m**" for meter and not "**M**", which you will see later to represent solution concentration, something very different from length. However, when it comes to volume, the base unit "liter" is abbreviated as "**L**" and not "l". So we would write 3.5 milliliters as $\mathbf{3.5\ mL}$.

As a practical matter, whenever possible you should express the units in a small and manageable number. If you are measuring the weight of a material that weighs $\mathbf{6.5\ kg}$, this is easier than saying it weighs $\mathbf{6500\ g}$ or $\mathbf{0.65\ dag}$. All three are correct, but the **kg** units in this case make for a small and easily managed number. However, if a specific problem needs grams instead of kilograms, go with the grams for consistency.

### ✔ Example 1.3.2: Unit Abbreviations

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kiloliter
b. microsecond
c. decimeter
d. nanogram

**Solutions**

Solutions to example explaining unit abbreviations.

| | Explanation | Answer |
|---|---|---|
| **a** | The prefix kilo means “1,000 ×,” so 1 kL equals 1,000 L | kL |
| **b** | The prefix micro implies 1/1,000,000th of a unit, so 1 µs equals 0.000001 s. | µs |
| **c** | The prefix deci means 1/10th, so 1 dm equals 0.1 m. | dm |
| **d** | The prefix nano means 1/1000000000, so a nanogram is equal to 0.000000001 g | ng |

**? Exercise 1.3.2**

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kilometer
b. milligram
c. nanosecond
d. centiliter

**Answer a**

km

**Answer b**

mg

**Answer c**

ns

**Answer d**

cL

## Scientific Notation

Chemists often work with numbers that are exceedingly large or small. For example, entering the mass in grams of a hydrogen atom into a calculator would require a display with at least 24 decimal places. A system called **scientific notation** avoids much of the tedium and awkwardness of manipulating numbers with large or small magnitudes. In scientific notation, these numbers are expressed in the form

$$N \times 10^{n} \tag{1.3.1}$$

where N is a number greater than or equal to 1 and less than 10 ($1 \le N < 10$), and $n$ is a positive or negative integer ($10^0 = 1$). The number 10 is called the base because it is this number that is raised to the power $n$. Although a base number may have values other than 10, the base number in scientific notation is always 10.

A simple way to convert numbers to scientific notation is to move the decimal point as many places to the left or right as needed to give a number from 1 to 10 (N). The magnitude of n is then determined as follows:

- If the decimal point is moved to the left $n$ places, $n$ is positive.
- If the decimal point is moved to the right $n$ places, $n$ is negative.

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Example 1.3.1.

### Example 1.3.1: Expressing Numbers in Scientific Notation

Convert each number to scientific notation.

a. 637.8
b. 0.0479
c. 7.86
d. 12,378
e. 0.00032
f. 61.06700
g. 2002.080
h. 0.01020

**Solution**

Solutions to example explaining how numbers look in scientific notation.

| | Explanation | Answer |
|---|---|---|
| **a** | To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the left: 637.8<br>Because the decimal point was moved two places to the left, n = 2. | $6.378 \times 10^{2}$ |
| **b** | To convert 0.0479 to a number from 1 to 10, we move the decimal point two places to the right: 0.0479<br>Because the decimal point was moved two places to the right, n = −2. | $4.79 \times 10^{-2}$ |
| **c** | This is usually expressed simply as 7.86. (Recall that $10^{0} = 1$.) | $7.86 \times 10^{0}$ |
| **d** | Because the decimal point was moved four places to the left, n = 4. | $1.2378 \times 10^{4}$ |
| **e** | Because the decimal point was moved four places to the right, n = −4. | $3.2 \times 10^{-4}$ |
| **f** | Because the decimal point was moved one place to the left, n = 1. | $6.106700 \times 10^{1}$ |
| **g** | Because the decimal point was moved three places to the left, n = 3. | $2.002080 \times 10^{3}$ |
| **h** | Because the decimal point was moved two places to the right, n = -2. | $1.020 \times 10^{-2}$ |

## Scientific Notation: Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N. Example **1.3.2** illustrates how to do this.

### Example 1.3.2: Expressing Sums and Differences in Scientific Notation

Carry out the appropriate operation and then express the answer in scientific notation.

a. $(1.36 \times 10^{2}) + (4.73 \times 10^{3})$

b. $(6.923 \times 10^{-3}) - (8.756 \times 10^{-4})$

**Solution**

Solution to example explaining how sums and differences look in scientific notation.

| | Explanation | Answer |
|---|---|---|
| **a** | Both exponents must have the same value, so these numbers are converted to either $(1.36 \times 10^2) + (47.3 \times 10^2) = (1.36 + 47.3) \times 10^2 = 48.66 \times 10^2$ or $(0.136 \times 10^3) + (4.73 \times 10^3) = (0.136 + 4.73) \times 10^3) = 4.87 \times 10^3$. Choosing either alternative gives the same answer, reported to two decimal places: In converting 48.66 × $10^2$ to scientific notation, $n$ has become more positive by 1 because the value of $N$ has decreased. | $4.87 \times 10^3$ |
| **b** | Converting the exponents to the same value gives either $(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3}) = (6.923 - 0.8756) \times 10^{-3}$ or $(69.23 \times 10^{-4}) - (8.756 \times 10^{-4}) = (69.23 - 8.756) \times 10^{-4} = 60.474 \times 10^{-4}$. In converting 60.474 × $10^{-4}$ to scientific notation, $n$ has become more positive by 1 because the value of $N$ has decreased. | $6.047 \times 10^{-3}$ |

## Scientific Notation: Multiplication and Division

When multiplying numbers expressed in scientific notation, we multiply the values of $N$ and add together the values of $n$. Conversely, when dividing, we divide $N$ in the dividend (the number being divided) by $N$ in the divisor (the number by which we are dividing) and then subtract n in the divisor from n in the dividend. In contrast to addition and subtraction, the exponents do not have to be the same in multiplication and division. Examples of problems involving multiplication and division are shown in Example **1.3.3**.

### Example 1.3.3: Expressing Products and Quotients in Scientific Notation

Perform the appropriate operation and express your answer in scientific notation.

a. $[(6.022 \times 10^{23})(6.42 \times 10^{-2})$

b. $\dfrac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}}$

c. $\dfrac{(6.63 \times 10^{-34})(6.0 \times 10)}{8.52 \times 10^{-2}}$

**Solution**

Solutions to example explaining how products and quotients look in scientific notation.

| | Explanation | Answer |
|---|---|---|
| **a** | In multiplication, we add the exponents: $$(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23+(-2)]} = 38.7 \times 10^{21}$$ In converting $38.7 \times 10^{21}$ to scientific notation, $n$ has become more positive by 1 because the value of $N$ has decreased. | $3.87 \times 10^{22}$ |
| **b** | In division, we subtract the exponents: $$\frac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}} = \frac{1.67}{9.12} \times 10^{[-24-(-28)]} = 0.183 \times 10^{4}$$ In converting $0.183 \times 10^{4}$ to scientific notation, $n$ has become more negative by 1 because the value of $N$ has increased. | $1.83 \times 10^{3}$ |
| **c** | This problem has both multiplication and division: $$\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \frac{39.78}{8.52} \times 10^{[-34+1-(-2)]}$$ | $4.7 \times 10^{-31}$ |

## Key Takeaways

- Identifying a quantity properly requires both a number and a unit.
- Metric prefixes derive from Latin or Greek terms. The prefixes are used to make the units manageable.
- The SI system is based on multiples of ten. There are seven basic units in the SI system. Five of these units are commonly used in chemistry.

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# 1.4: Significant Figures - Writing Numbers to Reflect Precision

**Learning Objectives**

- Identify the number of significant figures in a reported value.
- Describe uncertainty in measurements, accuracy, and precision.

The **significant figures** in a measurement consist of all the certain digits in that measurement plus one uncertain or estimated digit. In the ruler illustration below, the bottom ruler gave a length with 2 significant figures, while the top ruler gave a length with 3 significant figures. In a correctly reported measurement, the final digit is significant but not certain. Insignificant digits are not reported. With either ruler, it would not be possible to report the length at $2.553\ \text{cm}$ as there is no possible way that the thousandths digit could be estimated. The 3 is not significant and would not be reported.

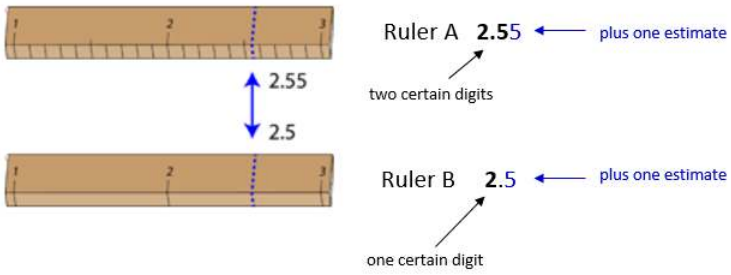



Figure 1.4.1: Measurement with two different rulers.
Ruler A's measurement can be rounded to 2.55, with 2 certain digits, while Ruler B's measurement of 2.5 has 1 certain digit

## Measurement Uncertainty

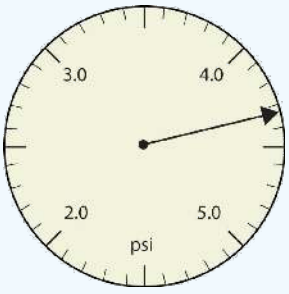
Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest $0.1\ \text{g}$, other highly sensitive balances are capable of measuring to the nearest $0.001\ \text{g}$ or even better. Many measuring tools such as rulers and graduated cylinders have small lines which need to be carefully read in order to make a measurement. Figure 1.4.1 shows two rulers making the same measurement of an object (indicated by the blue arrow).

With either ruler, it is clear that the length of the object is between $2$ and $3\ \text{cm}$. The bottom ruler contains no millimeter markings. With that ruler, the tenths digit can be estimated and the length may be reported as $2.5\ \text{cm}$. However, another person may judge that the measurement is $2.4\ \text{cm}$ or perhaps $2.6\ \text{cm}$. While the 2 is known for certain, the value of the tenths digit is uncertain.

The top ruler contains marks for tenths of a centimeter (millimeters). Now the same object may be measured as $2.55\ \text{cm}$. The measurer is capable of estimating the hundredths digit because he can be certain that the tenths digit is a 5. Again, another measurer may report the length to be $2.54\ \text{cm}$ or $2.56\ \text{cm}$. In this case, there are two certain digits (the 2 and the 5), with the hundredths digit being uncertain. Clearly, the top ruler is a superior ruler for measuring lengths as precisely as possible.

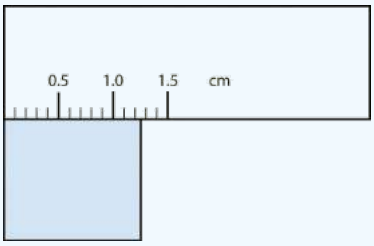
**Example 1.4.1: Reporting Measurements to the Proper Number of Significant Figures**

Use each diagram to report a measurement to the proper number of significant figures.




a.

b.




Ruler measuring a rectangle in units of centimeters, with the rectangle's edge between 1.2 and 1.3 cm marks

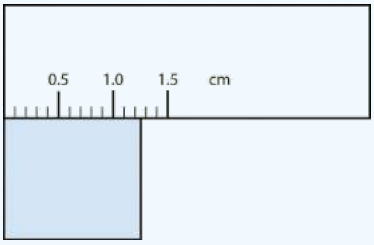
## Solutions

Solutions to Example 2.3.1

| | Explanation | Answer |
|---|---|---|
| **a.** | The arrow is between 4.0 and 5.0, so the measurement is at least 4.0. The arrow is between the third and fourth small tick marks, so it's at least 0.3. We will have to estimate the last place. It looks like about one-third of the way across the space, so let us estimate the hundredths place as 3. The symbol psi stands for "pounds per square inch" and is a unit of pressure, like air in a tire. The measurement is reported to three significant figures. | 4.33 psi |
| **b.** | The rectangle is at least 1.0 cm wide but certainly not 2.0 cm wide, so the first significant digit is 1. The rectangle's width is past the second tick mark but not the third; if each tick mark represents 0.1, then the rectangle is at least 0.2 in the next significant digit. We have to estimate the next place because there are no markings to guide us. It appears to be about halfway between 0.2 and 0.3, so we will estimate the next place to be a 5. Thus, the measured width of the rectangle is 1.25 cm. The measurement is reported to three significant figures. | 1.25 cm |

### ? Exercise 1.4.1

What would be the reported width of this rectangle?



**Answer**

1.25 cm

When you look at a reported measurement, it is necessary to be able to count the number of significant figures. The table below details the rules for determining the number of significant figures in a reported measurement. For the examples in the table, assume that the quantities are correctly reported values of a measured quantity.

Table 1.4.1: Significant Figure Rules

| Rule | Examples |
|---|---|
| 1. All nonzero digits in a measurement are significant. | • 237 has three significant figures.<br>• 1.897 has four significant figures. |
| 2. Zeros that appear between other nonzero digits (middle zeros) are always significant. | • 39,004 has five significant figures.<br>• 5.02 has three significant figures. |
| 3. Zeros that appear in front of all of the nonzero digits are called leading zeros. Leading zeros are never significant. | • 0.008 has one significant figure.<br>• 0.000416 has three significant figures. |
| 4. Zeros that appear after all nonzero digits are called trailing zeros. A number with trailing zeros that lacks a decimal point may or may not be significant. **Use scientific notation to indicate the appropriate number of significant figures.** | • 1400 is ambiguous.<br>  ○ $1.4 \times 10^3$ has two significant figures.<br>  ○ $1.40 \times 10^3$ three significant figures.<br>  ○ $1.400 \times 10^3$ has four significant figures. |
| 5. Trailing zeros in a number with a decimal point are significant. This is true whether the zeros occur before or after the decimal point. | • 620.0 has four significant figures.<br>• 19.000 has five significant figures. |

## Exact Numbers

Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000…). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

**Example 1.4.2**

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

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

Solution

Solution to Example 2.3.2

| | Explanation | Answer |
|---|---|---|
| a | All three numbers are significant (rule 1). | 5.87, three significant figures |
| b | The leading zeros are not significant (rule 3). The 3 and the 1 are significant (rule 1). | 0.031, two significant figures |
| c | The 5, the 2 and the 9 are significant (rule 1). The trailing zero is also significant (rule 5). | 52.90, four significant figures |
| d | The leading zeros are not significant (rule 3). The 2 and the 1 are significant (rule 1) and the middle zeros are also significant (rule 2). | 00.2001, four significant figures |
| e | The number is ambiguous. It could have one, two or three significant figures. | 500, ambiguous |
| f | The 6 is a counting number. A counting number is an exact number. | 6, infinite |

**? Exercise 1.4.2**

Give the number of significant figures in each.

a. 36.7 m
b. 0.006606 s
c. 2,002 kg
d. 306,490,000 people
e. 3,800 g

**Answer a**

three significant figures

**Answer b**

four significant figures

**Answer c**

four significant figures

**Answer d**

infinite (exact number)

**Answer e**

Ambiguous, could be two, three or four significant figures.

## Accuracy and Precision

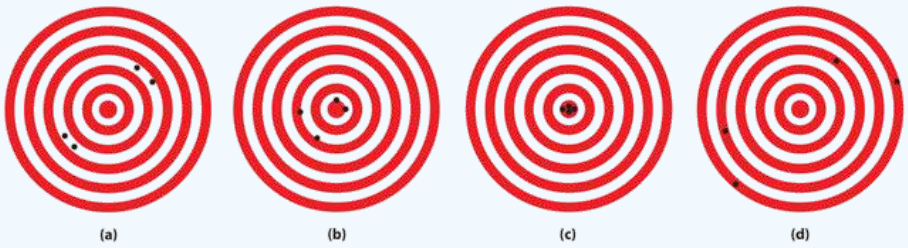
Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal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



Video **1.4.1**: Difference between precision and accuracy.

**Example 1.4.3**

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




Which target shows

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

**Solution**

a. Set a is precise, but inaccurate.
b. Set c is both precise and accurate.
c. Set d is neither precise nor accurate.

## Summary

Uncertainty exists in all measurements. The degree of uncertainty is affected in part by the quality of the measuring tool. Significant figures give an indication of the certainty of a measurement. Rules allow decisions to be made about how many digits to use in any given situation.

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# 1.5: Significant Figures in Calculations

**Learning Objectives**

- Use rounding rules to report a value with the correct number of significant figures.
- Use significant figures correctly in arithmetical operations.

## Rounding

Before dealing with the specifics of the rules for determining the significant figures in a calculated result, we need to be able to round numbers correctly. To **round** a number, first decide how many significant figures the number should have. Once you know that, round to that many digits, starting from the left. If the number immediately to the right of the last significant digit is less than 5, it is dropped and the value of the last significant digit remains the same. If the number immediately to the right of the last significant digit is greater than or equal to 5, the last significant digit is increased by 1.

Consider the measurement $207.518\ \text{m}$. Right now, the measurement contains six significant figures. How would we successively round it to fewer and fewer significant figures? Follow the process as outlined in Table 1.5.1.

Table 1.5.1: Rounding examples

| Number of Significant Figures | Rounded Value | Reasoning |
|---|---|---|
| 6 | 207.518 | All digits are significant |
| 5 | 207.52 | 8 rounds the 1 up to 2 |
| 4 | 207.5 | 2 is dropped |
| 3 | 208 | 5 rounds the 7 up to 8 |
| 2 | 210 | 8 is replaced by a 0 and rounds the 0 up to 1 |
| 1 | 200 | 1 is replaced by a 0 |

Notice that the more rounding that is done, the less reliable the figure is. An approximate value may be sufficient for some purposes, but scientific work requires a much higher level of detail.

It is important to be aware of significant figures when you are mathematically manipulating numbers. For example, dividing 125 by 307 on a calculator gives 0.4071661238… to an infinite number of digits. But do the digits in this answer have any practical meaning, especially when you are starting with numbers that have only three significant figures each? When performing mathematical operations, there are two rules for limiting the number of significant figures in an answer—one rule is for addition and subtraction, and one rule is for multiplication and division.

> *In operations involving significant figures, the answer is reported in such a way that it reflects the reliability of the **least precise** operation. An answer is no more precise than the least precise number used to get the answer.*

## Multiplication and Division

For multiplication or division, the rule is to count the number of significant figures in each number being multiplied or divided and then limit the significant figures in the answer to the lowest count. An example is as follows:

$$\underbrace{38.65}_{\text{4 sig figs}} \times \underbrace{105.93}_{\text{5 sig figs}} = \underbrace{4{,}094.1945}_{\text{reduce to 4 sig figs}}$$

The final answer, limited to four significant figures, is 4,094. The first digit dropped is 1, so we do not round up.

Scientific notation provides a way of communicating significant figures without ambiguity. You simply include all the significant figures in the leading number. For example, the number 450 has two significant figures and would be written in scientific notation as $4.5 \times 10^2$, whereas 450.0 has four significant figures and would be written as $4.500 \times 10^2$. In scientific notation, all significant figures are listed explicitly.

### Example 1.5.1

Write the answer for each expression using scientific notation with the appropriate number of significant figures.

a. $23.096 \times 90.300$
b. $125 \times 9.000$

#### Solution

a

Table with two columns and 1 row. The first column on the left is labeled, Explanation, and underneath in the row is an explanation. The second column is labeled, Answer, and underneath in the row is an answer.

| Explanation | Answer |
|---|---|
| The calculator answer is 2,085.5688, but we need to round it to five significant figures. Because the first digit to be dropped (in the tenths place) is greater than 5, we round up to 2,085.6. | $2.0856 \times 10^3$ |

b

Table with two columns and 1 row. The first column on the left is labeled, Explanation, and underneath in the row is an explanation. The second column is labeled, Answer, and underneath in the row is an answer.

| Explanation | Answer |
|---|---|
| The calculator gives 1,125 as the answer, but we limit it to three significant figures. | $1.13 \times 10^3$ |

## Addition and Subtraction

How are significant figures handled in calculations? It depends on what type of calculation is being performed. If the calculation is an addition or a subtraction, the rule is as follows: limit the reported answer to the rightmost column that all numbers have significant figures in common. For example, if you were to add 1.2 and 4.71, we note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

$$\begin{array}{r} 1.2 \\ \underline{4.41} \\ 5.61 \end{array}$$

↑ limit final answer to the tenths column: 5.6

We drop the last digit—the 1—because it is not significant to the final answer.

The dropping of positions in sums and differences brings up the topic of rounding. Although there are several conventions, in this text we will adopt the following rule: the final answer should be rounded up if the first dropped digit is 5 or greater, and rounded down if the first dropped digit is less than 5.

77.2
10.46
87.66
↑ limit final answer to the tenths column and round up: 87.7

## Example 1.5.2

a. 13.77 + 908.226
b. 1,027 + 611 + 363.06

### Solution

a

Table with two columns and 1 row. The first column on the left is labeled, Explanation, and underneath in the row is an explanation. The second column is labeled, Answer, and underneath in the row is an answer.

| Explanation | Answer |
|---|---|
| The calculator answer is 921.996, but because 13.77 has its farthest-right significant figure in the hundredths place, we need to round the final answer to the hundredths position. Because the first digit to be dropped (in the thousandths place) is greater than 5, we round up to 922.00 | $922.00 = 9.2200 \times 10^2$ |

b

Table with two columns and 1 row. The first column on the left is labeled, Explanation, and underneath in the row is an explanation. The second column is labeled, Answer, and underneath in the row is an answer.

| Explanation | Answer |
|---|---|
| The calculator gives 2,001.06 as the answer, but because 611 and 1027 has its farthest-right significant figure in the ones place, the final answer must be limited to the ones position. | $2,001.06 = 2.001 \times 10^3$ |

## Exercise 1.5.2

Write the answer for each expression using scientific notation with the appropriate number of significant figures.

a. 217 ÷ 903
b. 13.77 + 908.226 + 515
c. 255.0 − 99
d. 0.00666 × 321

**Answer a:**

$0.240 = 2.40 \times 10^{-1}$

**Answer b:**

$1,437 = 1.437 \times 10^3$

**Answer c:**

$156 = 1.56 \times 10^2$

**Answer d:**

$2.14 = 2.14 \times 10^0$

Remember that calculators do not understand significant figures. *You* are the one who must apply the rules of significant figures to a result from your calculator.

## Calculations Involving Multiplication/Division and Addition/Subtraction

In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding can compound inaccuracies, intermediate rounding needs to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.



Video **1.5.1**: Significant figures in mixed operations (https://www.youtube.com/watch?v=yBntMndXQWA).



Video **1.5.2**: https://www.youtube.com/watch?v=__csP0NtlGI

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

**Example 1.5.3**

a. 2(1.008 g) + 15.99 g

b. 137.3 s + 2(35.45 s)

c. $\frac{118.7g}{2} - 35.5g$

Solution

a.

Table with two columns and 1 row. The first column on the left is labeled, Explanation, and underneath in the row is an explanation for multiplication first. The second column is labeled, Answer, and underneath in the row is an answer.

| Explanation | Answer |
|---|---|
| 2(1.008 g) + 15.99 g =<br><br>Perform multiplication first.<br>2 (1.008 g *4 sig figs*) = **2.016 g** *4 sig figs*<br>The number with the least number of significant figures is 1.008 g; *the number 2 is an exact number and therefore has an infinite number of significant figures.*<br><br>**Then, perform the addition.**<br>**2.016 g** *thousandths place* + 15.99 g *hundredths place (least precise)* = 18.006 g<br><br>**Round the final answer.**<br>Round the final answer to the hundredths place since 15.99 has its farthest right significant figure in the hundredths place (least precise). | 18.01 g (rounding up) |

**b.**

Table with two columns and 1 row. The first column on the left is labeled, Explanation, and underneath in the row is an explanation for multiplication first. The second column is labeled, Answer, and underneath in the row is an answer.

| Explanation | Answer |
|---|---|
| 137.3 s + 2(35.45 s) =<br><br>**Perform multiplication first.**<br>2(35.45 s *4 sig figs*) = **70.90 s** *4 sig figs*<br>The number with the least number of significant figures is 35.45; *the number 2 is an exact number and therefore has an infinite number of significant figures.*<br><br>**Then, perform the addition.**<br>137.3 s *tenths place (least precise)* + **70.90 s** *hundredths place* = 208.20 s<br><br>**Round the final answer.**<br>Round the final answer to the tenths place based on 137.3 s. | 208.2 s |

**c.**

Table with two columns and 1 row. The first column on the left is labeled, Explanation, and underneath in the row is an explanation for division first. The second column is labeled, Answer, and underneath in the row is an answer.

| Explanation | Answer |
| --- | --- |
| $\frac{118.7g}{2} - 35.5g =$<br>**Perform division first.**<br>$\frac{118.7g}{2}$ *4 sig figs* = **59.35 g** *4 sig figs*<br>The number with the least number of significant figures is 118.7 g; *the number 2 is an exact number and therefore has an infinite number of significant figures.*<br>**Perform subtraction next.**<br>**59.35 g** *hundredths place* − 35.5 g *tenths place (least precise)* = 23.85 g<br>**Round the final answer.**<br>Round the final answer to the tenths place based on 35.5 g. | 23.9 g (rounding up) |

**? Exercise 1.5.3**

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

a. 5(1.008s) - 10.66 s
b. 99.0 cm+ 2(5.56 cm)

**Answer a**

-5.62 s

**Answer b**

110.2 cm

## Summary

- Rounding
  - If the number to be dropped is greater than or equal to 5, increase the number to its left by 1 (e.g. 2.9699 rounded to three significant figures is 2.97).
  - If the number to be dropped is less than 5, there is no change (e.g. 4.00443 rounded to four significant figures is 4.004).
- The rule in multiplication and division is that the final answer should have the same number of significant figures as there are in the number with the fewest significant figures.
- The rule in addition and subtraction is that the answer is given the same number of decimal places as the term with the fewest decimal places.

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# 1.6: Problem Solving - Unit Conversions and Estimating Answers

**Learning Objectives**

- Convert a value reported in one unit to a corresponding value in a different unit.

The ability to convert from one unit to another is an important skill. For example, a nurse with 50 mg aspirin tablets who must administer 0.2 g of aspirin to a patient needs to know that 0.2 g equals 200 mg, so 4 tablets are needed. Fortunately, there is a simple way to convert from one unit to another.

## Conversion Factors

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

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

or

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

Suppose we divide both sides of the equation by 1 m (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:

$$\text{same quantity} \left\langle \frac{100\ \text{cm}}{1\ \text{m}} = 1 \right.$$

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. A fraction that has equivalent quantities in the numerator and the denominator but expressed in *different units* is called a **conversion factor**.

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:

$$\frac{3.55}{1} \times \frac{100\ \text{cm}}{1} = 355\ \text{cm} \tag{1.6.1}$$

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:

$$\text{quantity (in old units)} \times \text{conversion factor} = \text{quantity (in new units)}$$

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 (Equation 1.6.1), 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 1.6.1 shows a **concept map** for constructing a proper conversion.

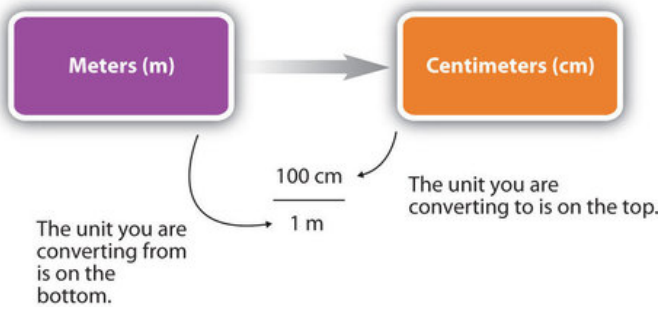



Figure 1.6.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Meters converted to centimeters. A fraction showing 100 cm over 1 m. The unit you convert to is on top, and the unit you convert from is on bottom.

## Significant Figures in Conversions

How do conversion factors affect the determination of significant figures? Numbers in conversion factors based on prefix changes, such as kilograms to grams, are *not* considered in the determination of significant figures in a calculation because the numbers in such conversion factors are exact. **Exact numbers** are *defined* or *counted* numbers, not measured numbers, and can be considered as having an infinite number of significant figures. (In other words, 1 kg is exactly 1,000 g, by the definition of kilo-.) Counted numbers are also exact. If there are 16 students in a classroom, the number 16 is exact. In contrast, conversion factors that come from measurements (such as density, as we will see shortly) or are approximations have a limited number of significant figures and should be considered in determining the significant figures of the final answer.

### Example 1.6.1

a. The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?
b. A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?

**Solution**

a. We start with what we are given, 4.7 L. We want to change the unit from liters to milliliters. There are 1,000 mL in 1 L. From this relationship, we can construct two conversion factors:

$$\frac{1\ \text{L}}{1,000\ \text{mL}} \quad \text{or} \quad \frac{1,000\ \text{mL}}{1\ \text{L}}$$

We use the conversion factor that will cancel out the original unit, liters, and introduce the unit we are converting to, which is milliliters. The conversion factor that does this is the one on the right.



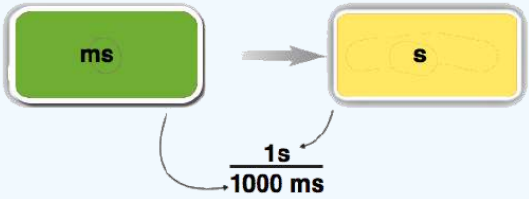

$$4.7 \cancel{L} \times \frac{1,000 \text{ mL}}{1 \cancel{L}} = 4,700 \text{ mL}$$

Because the numbers in the conversion factor are exact, we do not consider them when determining the number of significant figures in the final answer. Thus, we report two significant figures in the final answer.

b. We can construct two conversion factors from the relationships between milliseconds and seconds:

$$\frac{1,000 \text{ ms}}{1 \text{ s}} \text{ or } \frac{1 \text{ s}}{1,000 \text{ ms}}$$

To convert 18 ms to seconds, we choose the conversion factor that will cancel out milliseconds and introduce seconds. The conversion factor on the right is the appropriate one. We set up the conversion as follows:




$$18 \cancel{\text{ms}} \times \frac{1 \text{ s}}{1,000 \cancel{\text{ms}}} = 0.018 \text{ s}$$

The conversion factor's numerical values do not affect our determination of the number of significant figures in the final answer.

**? Exercise 1.6.1**

Perform each conversion.

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

**Answer a**

$$101,000 \cancel{\text{ns}} \times \frac{1 \text{ s}}{1,000,000,000 \cancel{\text{ns}}} = 0.000101 \text{ s}$$

**Answer b**

$$32.08 \cancel{\text{kg}} \times \frac{1,000 \text{ g}}{1 \cancel{\text{kg}}} = 32,080 \text{ g}$$

## Conversion Factors From Different Units

Conversion factors can also be constructed for converting between different kinds of units. For example, density can be used to convert between the mass and the volume of a substance. Consider mercury, which is a liquid at room temperature and has a density of 13.6 g/mL. The density tells us that 13.6 g of mercury have a volume of 1 mL. We can write that relationship as follows:

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

$$\frac{13.6\ \text{g}}{1\ \text{mL}} \text{ and } \frac{1\ \text{mL}}{13.6\ \text{g}}$$

Which one do we use? It depends, as usual, on the units we need to cancel and introduce. For example, suppose we want to know the mass of 16 mL of mercury. We would use the conversion factor that has milliliters on the bottom (so that the milliliter unit cancels) and grams on top so that our final answer has a unit of mass:

$$16\ \cancel{\text{mL}} \times \frac{13.6\ \text{g}}{1\ \cancel{\text{mL}}} = 217.6\ \text{g}$$

$$\approx 220\ \text{g}$$

In the last step, we limit our final answer to two significant figures because the volume quantity has only two significant figures; the 1 in the volume unit is considered an exact number, so it does not affect the number of significant figures. The other conversion factor would be useful if we were given a mass and asked to find volume, as the following example illustrates.

Density can be used as a conversion factor between mass and volume.

### Example 1.6.2: Mercury Thermometer

A mercury thermometer for measuring a patient's temperature contains 0.750 g of mercury. What is the volume of this mass of mercury?

**Solution**

Because we are starting with grams, we want to use the conversion factor that has grams in the denominator. The gram unit will cancel algebraically, and milliliters will be introduced in the numerator.

$$0.750\ \cancel{\text{g}} \times \frac{1\ \text{mL}}{13.6\ \cancel{\text{g}}} = 0.055147\ldots\ \text{mL}$$

$$\approx 0.0551\ \text{mL}$$

We have limited the final answer to three significant figures.

### Exercise 1.6.2

What is the volume of 100.0 g of air if its density is 1.3 g/L?

**Answer**

$$100.0\ \cancel{\text{g}} \times \frac{1\ \text{L}}{1.3\ \cancel{\text{g}}} = 76.92307692\ \text{L} \approx 77\text{L}$$

Because the density (1.3 g/L) has only 2 significant figures, we are rounding off the final answer to 2 significant figures.

## Problem Solving With Multiple Conversions

Sometimes you will have to perform more than one conversion to obtain the desired unit. For example, suppose you want to convert 54.7 km into millimeters. You can either memorize the relationship between kilometers and millimeters, or you can do the conversion in two steps. Most people prefer to convert in steps.

To do a stepwise conversion, we first convert the given amount to the base unit. In this example, the base unit is meters. We know that there are 1,000 m in 1 km:

$$54.7\ \cancel{\text{km}} \times \frac{1,000\ \text{m}}{1\ \cancel{\text{km}}} = 54,700\ \text{m}$$

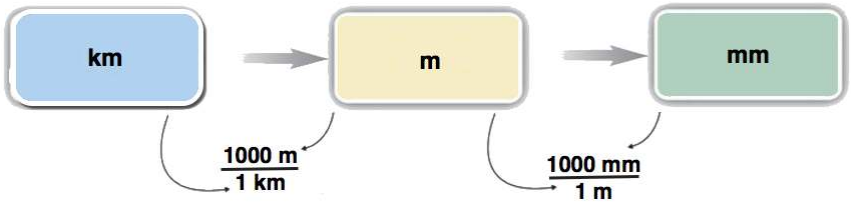
Then we take the result (54,700 m) and convert it to millimeters, remembering that there are $1,000\ \text{mm}$ for every $1\ \text{m}$:

$$54,700\ \cancel{\text{m}} \times \frac{1,000\ \text{mm}}{1\ \cancel{\text{m}}} = 54,700,000\ \text{mm}$$
$$= 5.47 \times 10^7\ \text{mm}$$

We have expressed the final answer in scientific notation.

As a shortcut, both steps in the conversion can be combined into a single, multistep expression:

### Concept Map




### Calculation

$$54.7\ \cancel{\text{km}} \times \frac{1,000\ \cancel{\text{m}}}{1\ \cancel{\text{km}}} \times \frac{1,000\ \text{mm}}{1\ \cancel{\text{m}}} = 54,700,000\ \text{mm}$$
$$= 5.47 \times 10^7\ \text{mm}$$

In each step, the previous unit is canceled and the next unit in the sequence is produced, each successive unit canceling out until only the unit needed in the answer is left.

Either method—one step at a time or all the steps together—is acceptable. If you do all the steps together, the restriction for the proper number of significant figures should be done after the last step. As long as the math is performed correctly, you should get the same answer no matter which method you use.

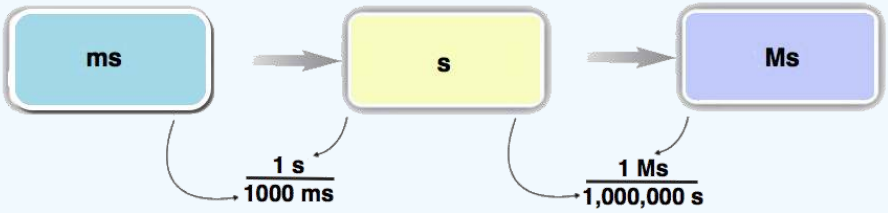
**Example 1.6.3**

Convert 58.2 ms to megaseconds in one multistep calculation.

**Solution**

First, convert the given unit (ms) to the base unit—in this case, seconds—and then convert seconds to the final unit, megaseconds:

**Concept Map**




To convert ms to s, put 1 s over 1000 ms in a fraction. To convert s to Ms, put 1 Ms over 1,000,000 s in a fraction.

**Calculation**

$$58.2\ \cancel{\text{ms}} \times \frac{1\cancel{\text{s}}}{1,000\ \cancel{\text{ms}}} \times \frac{1\ \text{Ms}}{1,000,000\ \cancel{\text{s}}} = 0.0000000582\ \text{Ms}$$
$$= 5.82 \times 10^{-8}\ \text{Ms}$$

Neither conversion factor affects the number of significant figures in the final answer.

## Exercise 1.6.3

Convert 43.007 mg to kilograms in one multistep calculation.

**Answer**

$$43.007\ \cancel{\text{mg}} \times \frac{1\ \cancel{\text{g}}}{1{,}000\ \cancel{\text{mg}}} \times \frac{1\ \text{kg}}{1{,}000\ \cancel{\text{g}}} = 0.000043007\ \text{kg}$$

$$= 4.3007 \times 10^{-5}\ \text{kg}$$

.

Neither conversion factor affects the number of significant figures in the final answer.

## Career Focus: Pharmacist

A pharmacist dispenses drugs that have been prescribed by a doctor. Although that may sound straightforward, pharmacists in the United States must hold a doctorate in pharmacy and be licensed by the state in which they work. Most pharmacy programs require four years of education in a specialty pharmacy school.

Pharmacists must know a lot of chemistry and biology so they can understand the effects that drugs (which are chemicals, after all) have on the body. Pharmacists can advise physicians on the selection, dosage, interactions, and side effects of drugs. They can also advise patients on the proper use of their medications, including when and how to take specific drugs properly. Pharmacists can be found in drugstores, hospitals, and other medical facilities.

Curiously, an outdated name for pharmacist is *chemist*, which was used when pharmacists formerly did a lot of drug preparation, or *compounding*. In modern times, pharmacists rarely compound their own drugs, but their knowledge of the sciences, including chemistry, helps them provide valuable services in support of everyone's health.

## Key Takeaway

- A unit can be converted to another unit of the same type with a conversion factor.

## Concept Review Exercises

1. How do you determine which quantity in a conversion factor goes in the denominator of the fraction?
2. State the guidelines for determining significant figures when using a conversion factor.
3. Write a concept map (a plan) for how you would convert $\mathbf{1.0 \times 10^{12}}$ *nano*liters (nL) to *kilo*liters (kL).

## Answers

1. The unit you want to cancel from the numerator goes in the denominator of the conversion factor.
2. Exact numbers that appear in many conversion factors do not affect the number of significant figures; otherwise, the normal rules of multiplication and division for significant figures apply.
3. Concept Map: Convert the given (nanoliters, nL) to liters; then convert liters to kiloliters.




1.0 times 10 to the 12th nL converts to 1000 Liters converts to 1 kiloLiter. One Liter is 1.0 times 10 to the 9th nL. One kiloLiter is 1000 Liters.

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# 1.7: Temperature and Density

**Learning Objective**

- Learn about the various temperature scales that are commonly used in chemistry.
- Define density and use it as a conversion factor.

There are other units in chemistry that are important, and we will cover others over the course of the entire book. One of the fundamental quantities in science is temperature. Temperature is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees, and there are several temperature scales in use. In the United States, the commonly used temperature scale is the *Fahrenheit scale* (symbolized by °F and spoken as "degrees Fahrenheit"). On this scale, the freezing point of liquid water (the temperature at which liquid water turns to solid ice) is 32°F, and the boiling point of water (the temperature at which liquid water turns to steam) is 212°F.

Science also uses other scales to express temperature. The Celsius scale (symbolized by °C and spoken as "degrees Celsius") is a temperature scale where 0°C is the freezing point of water and 100°C is the boiling point of water; the scale is divided into 100 divisions between these two landmarks and extended higher and lower. By comparing the Fahrenheit and Celsius scales, a conversion between the two scales can be determined:

$$^{\circ}\mathrm{C} = (^{\circ}\mathrm{F}\text{-}32) \times \tfrac{5}{9} \tag{1.7.1}$$

$$^{\circ}\mathrm{F} = (^{\circ}\mathrm{C} \times \tfrac{9}{5}) + 32 \tag{1.7.2}$$

**Example 1.7.1: Conversions**

a. What is 98.6 °F in degrees Celsius?
b. What is 25.0 °C in degrees Fahrenheit?

**Solution**

a. Using Equation 1.7.1, we have

$$\begin{aligned} ^{\circ}C &= (98.6 - 32) \times \frac{5}{9} \\ &= 66.6 \times \frac{5}{9} \\ &= 37.0^{\circ}C \end{aligned}$$

b. Using Equation 1.7.2, we have

$$\begin{aligned} ^{\circ}F &= \left(25.0 \times \frac{9}{5}\right) + 32 \\ &= 45.0 + 32 \\ &= 77.0^{\circ}F \end{aligned}$$

**Exercise 1.7.1**

a. Convert 0 °F to degrees Celsius.
b. Convert 212 °C to degrees Fahrenheit.

**Answer a**

−17.8 °C

**Answer b**

414 °F

The fundamental unit of temperature (another fundamental unit of science, bringing us to four) in SI is the kelvin (K). The Kelvin temperature scale (note that the name of the scale capitalizes the word *Kelvin*, but the unit itself is lowercase) uses degrees that are the same size as the Celsius degree, but the numerical scale is shifted up by 273.15 units. That is, the conversion between the Kelvin and Celsius scales is as follows:

$$K = {}^\circ C + 273.15$$

For most purposes, it is acceptable to use 273 instead of 273.15. Note that the Kelvin scale does not use the word *degrees*; a temperature of 295 K is spoken of as "two hundred ninety-five kelvins" and not "two hundred ninety-five degrees Kelvin."

The reason that the Kelvin scale is defined this way is because there exists a minimum possible temperature called absolute zero (zero kelvins). The Kelvin temperature scale is set so that 0 K is absolute zero, and temperature is counted upward from there. Normal room temperature is about 295 K, as seen in the following example.

### Example 1.7.2: Room Temperature

If normal room temperature is 72.0°F, what is room temperature in degrees Celsius and kelvin?

**Solution**

First, we use the formula to determine the temperature in degrees Celsius:

$$\begin{aligned} {}^\circ C &= (72.0 - 32) \times \frac{5}{9} \\ &= 40.0 \times \frac{5}{9} \\ &= 22.2^\circ C \end{aligned}$$

Then we use the appropriate formula above to determine the temperature in the Kelvin scale:

$$\begin{aligned} K &= 22.2^\circ C + 273.15 \\ &= 295.4 K \end{aligned}$$

So, room temperature is about 295 K.

### Exercise 1.7.2

What is 98.6°F on the Kelvin scale?

**Answer**

310.2 K

Figure **1.7.1** compares the three temperature scales. Note that science uses the Celsius and Kelvin scales almost exclusively; virtually no practicing chemist expresses laboratory-measured temperatures with the Fahrenheit scale. In fact, the United States is one of the few countries in the world that still uses the Fahrenheit scale on a daily basis. The other two countries are Liberia and Myanmar (formerly Burma). People driving near the borders of Canada or Mexico may pick up local radio stations on the other side of the border that express the daily weather in degrees Celsius, so do not get confused by their weather reports.

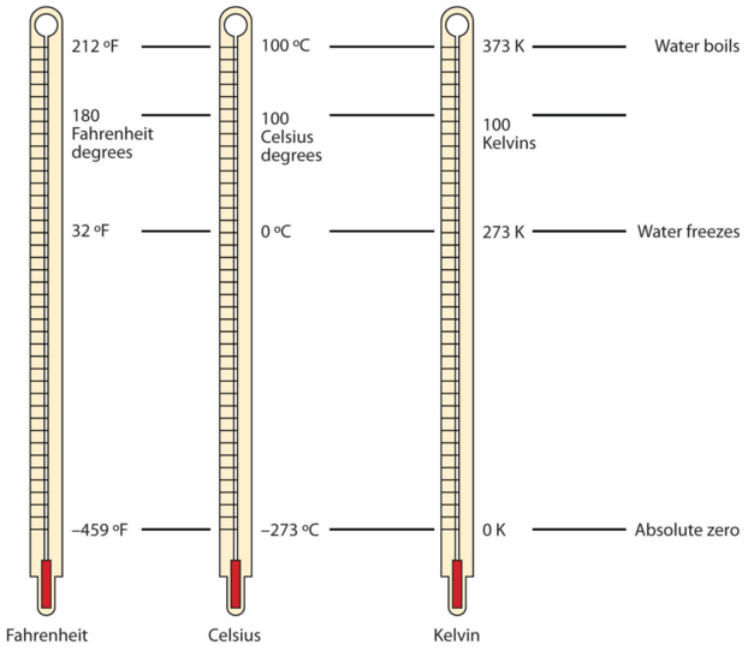



Figure 1.7.1: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales.

## Density

Density is a physical property that is defined as a substance's mass divided by its volume:

$$density = \frac{mass}{volume} \Rightarrow d = \frac{m}{v}$$

Density is usually a measured property of a substance, so its numerical value affects the significant figures in a calculation. Notice that density is defined in terms of two dissimilar units, mass and volume. That means that density overall has derived units, just like velocity. Common units for density include g/mL, g/cm$^3$, g/L, kg/L, and even kg/m$^3$. Densities for some common substances are listed in Table 1.7.1.

Table 1.7.1: Densities of Some Common Substances

| Substance | Density (g/mL or g/cm$^3$) |
|---|---|
| water | 1.0 |
| gold | 19.3 |
| mercury | 13.6 |
| air | 0.0012 |
| cork | 0.22–0.26 |
| aluminum | 2.7 |
| iron | 7.87 |

Because of how it is defined, density can act as a conversion factor for switching between units of mass and volume. For example, suppose you have a sample of aluminum that has a volume of 7.88 cm$^3$. How can you determine what mass of aluminum you have without measuring it? You can use the volume to calculate it. If you multiply the given volume by the known density (from Table 1.7.1), the volume units will cancel and leave you with mass units, telling you the mass of the sample:

$$7.88 \cancel{cm^3} \times \frac{2.7\,g}{\cancel{cm^3}} = 21\,g \text{ of aluminium}$$

where we have limited our answer to two significant figures.

### Example 1.7.3: Mercury

What is the mass of 44.6 mL of mercury?

**Solution**

Use the density from Table 1.7.1 "Densities of Some Common Substances" as a conversion factor to go from volume to mass:

$$44.6 \cancel{mL} \times \frac{13.6\,g}{\cancel{mL}} = 607\,g$$

The mass of the mercury is 607 g.

### Exercise 1.7.3

What is the mass of 25.0 $cm^3$ of iron?

**Answer**

197 g

Density can also be used as a conversion factor to convert mass to volume—but care must be taken. We have already demonstrated that the number that goes with density normally goes in the numerator when density is written as a fraction. Take the density of gold, for example:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

Although this was not previously pointed out, it can be assumed that there is a 1 in the denominator:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

That is, the density value tells us that we have 19.3 grams for every 1 milliliter of volume, and the 1 is an exact number. When we want to use density to convert from mass to volume, the numerator and denominator of density need to be switched—that is, we must take the *reciprocal* of the density. In so doing, we move not only the units, but also the numbers:

$$\frac{1}{d} = \frac{1\,mL}{19.3\,g}$$

This reciprocal density is still a useful conversion factor, but now the mass unit will cancel and the volume unit will be introduced. Thus, if we want to know the volume of 45.9 g of gold, we would set up the conversion as follows:

$$45.9 \cancel{g} \times \frac{1\,mL}{19.3\,\cancel{g}} = 2.38\,mL$$

Note how the mass units cancel, leaving the volume unit, which is what we are looking for.

### Example 1.7.4: Calculating Volume from Density

A cork stopper from a bottle of wine has a mass of 3.78 g. If the density of cork is 0.22 $g/cm^3$, what is the volume of the cork?

**Solution**

To use density as a conversion factor, we need to take the reciprocal so that the mass unit of density is in the denominator. Taking the reciprocal, we find:

$$\frac{1}{d} = \frac{1\,cm^3}{0.22\,g}$$

We can use this expression as the conversion factor. So

$$3.78 \cancel{g} \times \frac{1\,cm^3}{0.22\,\cancel{g}} = 17.2\,cm^3$$

**? Exercise 1.7.4**

What is the volume of 3.78 g of gold?

**Answer**

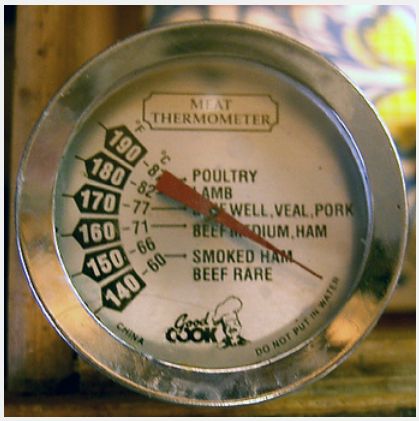
0.196 $cm^3$

Care must be used with density as a conversion factor. Make sure the mass units are the same, or the volume units are the same, before using density to convert to a different unit. Often, the unit of the given quantity must be first converted to the appropriate unit before applying density as a conversion factor.

**Food and Drink Application: Cooking Temperatures**

Because degrees Fahrenheit is the common temperature scale in the United States, kitchen appliances, such as ovens, are calibrated in that scale. A cool oven may be only 150°F, while a cake may be baked at 350°F and a chicken roasted at 400°F. The broil setting on many ovens is 500°F, which is typically the highest temperature setting on a household oven.

People who live at high altitudes, typically 2,000 ft above sea level or higher, are sometimes urged to use slightly different cooking instructions on some products, such as cakes and bread, because water boils at a lower temperature the higher in altitude you go, meaning that foods cook slower. For example, in Cleveland water typically boils at 212°F (100°C), but in Denver, the Mile-High City, water boils at about 200°F (93.3°C), which can significantly lengthen cooking times. Good cooks need to be aware of this.




*A meat thermometer with a dial. Notice the markings for Fahrenheit (outer scale) and Celsius (inner scale) temperatures. Recipes for cooking food in an oven can use very different numbers, depending on the country you're in. (CC BY2.0* Bev Sykes)

At the other end is pressure cooking. A pressure cooker is a closed vessel that allows steam to build up additional pressure, which increases the temperature at which water boils. A good pressure cooker can get to temperatures as high as 252°F (122°C); at these temperatures, food cooks much faster than it normally would. Great care must be used with pressure cookers because of the high pressure and high temperature. (When a pressure cooker is used to sterilize medical instruments, it is called an *autoclave*.)

Other countries use the Celsius scale for everyday purposes. Therefore, oven dials in their kitchens are marked in degrees Celsius. It can be confusing for US cooks to use ovens abroad—a 425°F oven in the United States is equivalent to a 220°C oven in other countries. These days, many oven thermometers are marked with both temperature scales.

## Key Takeaways

- Chemistry uses the Celsius and Kelvin scales to express temperatures.
- A temperature on the Kelvin scale is the Celsius temperature plus 273.15.
- The minimum possible temperature is absolute zero and is assigned 0 K on the Kelvin scale.
- Density relates the mass and volume of a substance.
- Density can be used to calculate volume from a given mass or mass from a given volume.

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# CHAPTER OVERVIEW

## 2: Atoms and Elements


2.1: The Elements
2.2: The Periodic Table
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2.4: Elements and Atomic Number
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2.10: Periodic Trends - Atomic Size and Ionization Energy


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# 2.1: The Elements

**Learning Objectives**

- Define a chemical element and give examples of the abundance of different elements.
- Represent a chemical element with a chemical symbol.

An element is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure **2.1.1** shows some of the chemical elements.



Figure **2.1.1**: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

## Abundance

The elements vary widely in abundance. In the universe as a whole, the most common element is hydrogen (about 90% of atoms), followed by helium (most of the remaining 10%). All other elements are present in relatively minuscule amounts, as far as we can detect.

Table **2.1.1**: Elemental Composition of Earth

| Earth's Crust | | Earth (overall) | |
|---|---|---|---|
| **Element** | **Percentage** | **Element** | **Percentage** |
| oxygen | 46.1 | iron | 34.6 |
| silicon | 28.2 | oxygen | 29.5 |
| aluminum | 8.23 | silicon | 15.2 |
| iron | 5.53 | magnesium | 12.7 |
| calcium | 4.15 | nickel | 2.4 |
| sodium | 2.36 | sulfur | 1.9 |
| magnesium | 2.33 | all others | 3.7 |
| potassium | 2.09 | | |
| titanium | 0.565 | | |
| hydrogen | 0.14 | | |
| phosphorus | 0.105 | | |
| all others | 0.174 | | |

Source: D. R. Lide, ed. *CRC Handbook of Chemistry and Physics*, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 14–17.

On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen, the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table **2.1.1** lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table **2.1.2** lists the relative abundances of elements in the human body. If you compare Table **2.1.1** and Table **2.1.2**, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table **2.1.1**; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table **2.1.2**: Elemental Composition of a Human Body

| Element | Percentage by Mass |
|---|---|
| oxygen | 61 |
| carbon | 23 |
| hydrogen | 10 |
| nitrogen | 2.6 |
| calcium | 1.4 |
| phosphorus | 1.1 |
| sulfur | 0.20 |
| potassium | 0.20 |
| sodium | 0.14 |
| chlorine | 0.12 |
| magnesium | 0.027 |
| silicon | 0.026 |
| iron | 0.006 |
| fluorine | 0.0037 |
| zinc | 0.0033 |
| all others | 0.174 |

Source: D. R. Lide, ed. *CRC Handbook of Chemistry and Physics*, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 7–24.

The relative amounts of elements in the body have less to do with their abundances on Earth than with their availability in a form we can assimilate. We obtain oxygen from the air we breathe and the water we drink. We also obtain hydrogen from water. On the other hand, although carbon is present in the atmosphere as carbon dioxide, and about 80% of the atmosphere is nitrogen, we obtain those two elements from the food we eat, not the air we breathe.

### LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

There is an element that we need more of in our bodies than is proportionately present in Earth's crust, and *this* element is not easily accessible. Phosphorus makes up 1.1% of the human body but only 0.105% of Earth's crust. We need phosphorus for our bones and teeth, and it is a crucial component of all living cells. Unlike carbon, which can be obtained from carbon dioxide through photosynthesis, there is no phosphorus compound present in our surroundings that can serve as a convenient source. Phosphorus, then, is nature's bottleneck. Its availability limits the amount of life our planet can sustain.

Higher forms of life, such as humans, can obtain phosphorus by selecting a proper diet (plenty of protein); but lower forms of life, such as algae, must absorb it from the environment. When phosphorus-containing detergents were introduced in the 1950s, wastewater from normal household activities greatly increased the amount of phosphorus available to algae and other plant life. Lakes receiving this wastewater experienced sudden increases in growth of algae. When the algae died, concentrations of bacteria that ate the dead algae increased. Because of the large bacterial concentrations, the oxygen content of the water dropped, causing fish to die in large numbers. This process, called *eutrophication*, is considered a negative environmental impact.

Today, many detergents are made without phosphorus so the detrimental effects of eutrophication are minimized. You may even see statements to that effect on detergent boxes. It can be sobering to realize how much impact a single element can have on life—or the ease with which human activity can affect the environment.

## Names and Symbols

Each element has a name. Some of these names date from antiquity, while others are quite new. Today, the names for new elements are proposed by their discoverers but must be approved by the International Union of Pure and Applied Chemistry, an international organization that makes recommendations concerning all kinds of chemical terminology.

> *Today, new elements are usually named after famous scientists.*

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table **2.1.3** lists the names and symbols of some of the most familiar elements.

Table **2.1.3**: Element Names and Symbols

| | | | |
|---|---|---|---|
| aluminum | Al | magnesium | Mg |
| argon | Ar | manganese | Mn |
| arsenic | As | mercury | Hg* |
| barium | Ba | neon | Ne |
| bismuth | Bi | nickel | Ni |
| boron | B | nitrogen | N |
| bromine | Br | oxygen | O |
| calcium | Ca | phosphorus | P |
| carbon | C | platinum | Pt |
| chlorine | Cl | potassium | K* |
| chromium | Cr | silicon | Si |
| copper | Cu* | silver | Ag* |
| fluorine | F | sodium | Na* |
| gold | Au* | strontium | Sr |
| helium | He | sulfur | S |
| hydrogen | H | tin | Sn* |
| iron | Fe | tungsten | W† |
| iodine | I | uranium | U |
| lead | Pb* | zinc | Zn |
| lithium | Li | zirconium | Zr |

*The symbol comes from the Latin name of element.

†The symbol for tungsten comes from its German name—*wolfram*.

Element names in languages other than English are often close to their Latin names. For example, gold is *oro* in Spanish and *or* in French (close to the Latin *aurum*), tin is *estaño* in Spanish (compare to *stannum*), lead is *plomo* in Spanish and *plomb* in French (compare to *plumbum*), silver is *argent* in French (compare to *argentum*), and iron is *fer* in French and *hierro* in Spanish (compare to *ferrum*). The closeness is even more apparent in pronunciation than in spelling.

### Example 2.1.1

Write the chemical symbol for each element without consulting Table **2.1.3** "Element Names and Symbols".

a. bromine
b. boron
c. carbon
d. calcium
e. gold

**Answer a**

Br

**Answer b**

B

**Answer c**

C

**Answer d**

Ca

**Answer e**

Au

## Exercise 2.1.1

Write the chemical symbol for each element without consulting Table 2.1.3.

a. manganese
b. magnesium
c. neon
d. nitrogen
e. silver

**Answer a**

Mn

**Answer b**

Mg

**Answer c**

Ne

**Answer d**

N

**Answer e**

Ag

## Example 2.1.2

What element is represented by each chemical symbol?

a. Na
b. Hg
c. P
d. K
e. I

**Answer a**

sodium

**Answer b**

mercury

**Answer c**

phosphorus

**Answer d**

potassium

**Answer e**

iodine

**? Exercise 2.1.2**

What element is represented by each chemical symbol?

a. Pb
b. Sn
c. U
d. O
e. F

**Answer a**

lead

**Answer b**

tin

**Answer c**

uranium

**Answer d**

oxygen

**Answer e**

fluorine

## Concept Review Exercises

1. What is an element?
2. Give some examples of how the abundance of elements varies.
3. Why are chemical symbols so useful? What is the source of the letter(s) for a chemical symbol?

## Answers

1. An element is the basic chemical building block of matter; it is the simplest chemical substance.
2. Elements vary from being a small percentage to more than 30% of the atoms around us.
3. Chemical symbols are useful to concisely represent the elements present in a substance. The letters usually come from the name of the element.

## Key Takeaways

- All matter is composed of elements.
- Chemical elements are represented by a one- or two-letter symbol.

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# 2.2: The Periodic Table

**Learning Objectives**

- Explain how elements are organized into the periodic table.
- Describe how some characteristics of elements relate to their positions on the periodic table.

In the 19th century, many previously unknown elements were discovered, and scientists noted that certain sets of elements had similar chemical properties. For example, chlorine, bromine, and iodine react with other elements (such as sodium) to make similar compounds. Likewise, lithium, sodium, and potassium react with other elements (such as oxygen) to make similar compounds. Why is this so?

In 1864, Julius Lothar Meyer, a German chemist, organized the elements by atomic mass and grouped them according to their chemical properties. Later that decade, Dmitri Mendeleev, a Russian chemist, organized all the known elements according to similar properties. He left gaps in his table for what he thought were undiscovered elements, and he made some bold predictions regarding the properties of those undiscovered elements. When elements were later discovered whose properties closely matched Mendeleev's predictions, his version of the table gained favor in the scientific community. Because certain properties of the elements repeat on a regular basis throughout the table (that is, they are periodic), it became known as the periodic table.

> *Mendeleev had to list some elements out of the order of their atomic masses to group them with other elements that had similar properties.*

The **periodic table** is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure **2.2.1**. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

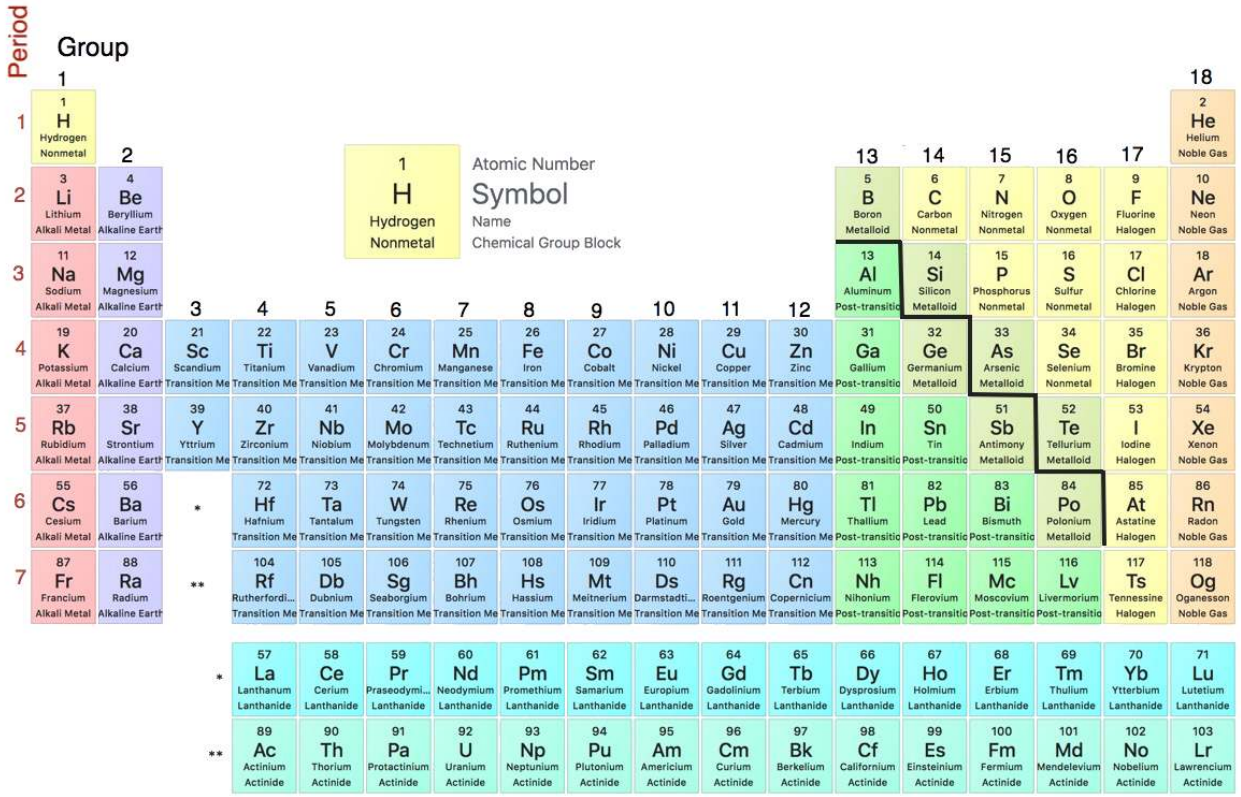



Figure **2.2.1**: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares). An interactive Periodic table can be found here.

Elements that have similar chemical properties are grouped in columns called **groups** (or families). As well as being numbered, some of these groups have names—for example, *alkali metals* (the first column of elements), *alkaline earth metals* (the second column of elements), *halogens* (the next-to-last column of elements), and *noble gases* (the last column of elements).

Each row of elements on the periodic table is called a **period**. Periods have different lengths; the first period has only 2 elements (hydrogen and helium), while the second and third periods have 8 elements each. The fourth and fifth periods have 18 elements each, and later periods are so long that a segment from each is removed and placed beneath the main body of the table.

## Metals, Nonmetals, and Metalloids

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure **2.2.2**. A metal is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A nonmetal is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure **2.2.2**, **metals** occupy the left three-fourths of the periodic table, while **nonmetals** (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

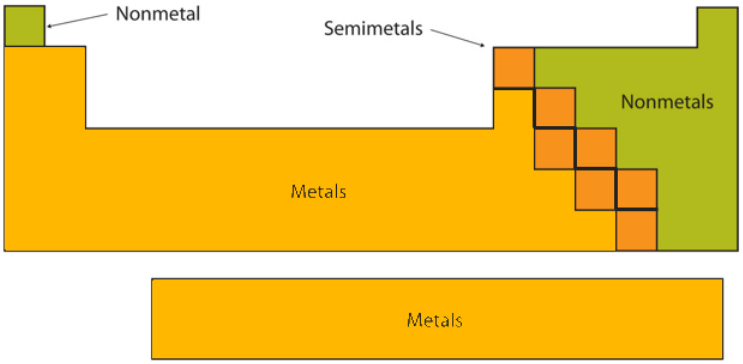



Figure **2.2.2**: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

### Example 2.2.1

Based on its position in the periodic table, classify each element below as metal, a nonmetal, or a metalloid.

a. Se
b. Mg
c. Ge

**Solution**

a. The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure **2.2.2**, 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.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be a metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

### Exercise 2.2.1

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

**Answer**

metal

## Representative, Transition, and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure **2.2.3**. The first two columns on the left (groups 1 and 2) and the last six columns on the right (groups 13-19) are called the **main group** or **representative** elements. The ten-column block between these columns (groups 3-12) contains the **transition metals**. The two rows beneath the main body of the periodic table contain the **inner transition metals**. The elements in these two rows are also referred to as, respectively, the lanthanide metals and the actinide metals.

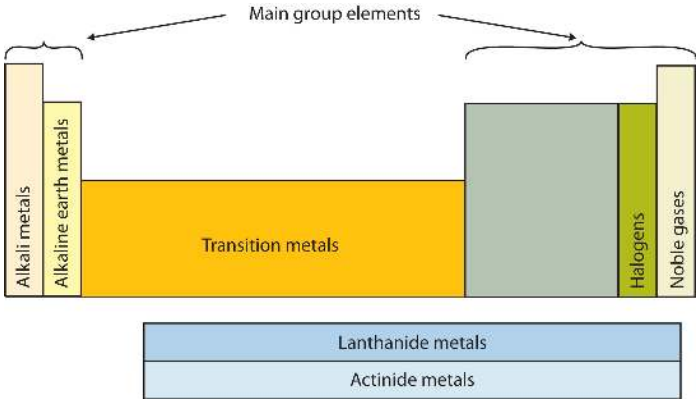



Figure **2.2.3**: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

### To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The most abundant non-main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal and the chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

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# 2.3: Atomic Theory and the Structure of Atoms

**Learning Objectives**

- State the modern atomic theory.
- Learn how atoms are constructed.
- Recognize and describe protons, neutrons, and electrons.

The smallest piece of an element that maintains the identity of that element is called an atom. Individual atoms are extremely small. It would take about fifty million atoms in a row to make a line that is 1 cm long. The period at the end of a printed sentence has several million atoms in it. Atoms are so small that it is difficult to believe that all matter is made from atoms-but it is.

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure **2.3.1**), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom 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 $5.4 \times 10^{-10}$ m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

Dalton studied the weights of various elements and compounds. He noticed that matter always combined in fixed ratios based on weight, or volume in the case of gases. Chemical compounds always contain the same proportion of elements by mass, regardless of amount, which provided further support for Proust's law of definite proportions. Dalton also observed that there could be more than one combination of two elements.

From his experiments and observations, as well as the work from peers of his time, Dalton proposed a new theory of the **atom**. This later became known as Dalton's **atomic theory**. 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.*

These concepts form the basis of chemistry. Although the word *atom* comes from a Greek word that means "indivisible," we understand now that atoms themselves are composed of smaller parts called **subatomic particles**. The first part to be discovered was the **electron**, a tiny subatomic particle with a negative charge. It is often represented as $e^-$, with the right superscript showing the negative charge. Later, two larger particles were discovered. The **proton**, a subatomic particle with a positive charge. is a more massive (but still tiny) subatomic particle with a positive charge, represented as $p^+$. The **neutron** is a subatomic particle with about the same mass as a proton but no charge. It is represented as either n or $n^0$. We now know that all atoms of all elements are composed of electrons, protons, and (with one exception) neutrons. Table **2.3.1** summarizes the properties of these three subatomic particles.

Table **2.3.1**: Properties of the Three Subatomic Particles

| Name | Symbol | Mass (approx.; g) | Mass (approx.; amu) | Charge |
|---|---|---|---|---|
| Proton | $p^+$ | $1.673 \times 10^{-24}$ | 1.0073 | 1+ |
| Neutron | n, $n^0$ | $1.675 \times 10^{-24}$ | 1.0087 | none |
| Electron | $e^-$ | $9.109 \times 10^{-28}$ | $5.486 \times 10^{-4}$ | 1− |

Atoms and subatomic particles are so small that it doesn't quite make sense to measure their masses in grams. A more useful unit to measure atomic mass is the **atomic mass unit (amu)**, where 1 amu = $1.660539 \times 10^{-24}$ g or one-twelfth of the mass of a carbon-12 atom. As you can see in the table above, the mass of 1 proton and 1 neutron are each 1 amu in this system. Carbon-12 contains six protons and six neutrons and is assigned a mass of exactly 12 amu.



Figure **2.3.1**: Electrons are much smaller than protons or neutrons. If an electron was the mass of a penny, a proton or a neutron would have the mass of a large bowling ball!

How are these subatomic particles arranged in atoms? They are not arranged at random. Experiments by Ernest Rutherford in England in the 1910's pointed to a nuclear model with atoms that has the protons and neutrons in a central nucleus with the electrons in orbit about the nucleus. The relatively massive protons and neutrons are collected in the center of an atom, in a region called the **nucleus** of the atom (plural *nuclei*). The electrons are outside the nucleus and spend their time orbiting in space about the nucleus. (Figure **2.3.2**). Because protons and neutrons are so massive compared to electrons, Table **2.3.1**, nearly all of the mass of an atom is contained in the nucleus.

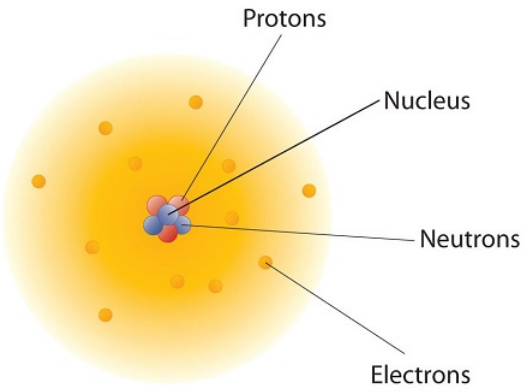



Figure **2.3.2**: The Structure of the Atom. Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.

## Atoms in Action

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. Moreover, they can even be used for making pretty images or as IBM research demonstrate in Video **2.3.1**, control of individual atoms can be use used create animations.



Video **2.3.1**: A Boy And His Atom - The World's Smallest Movie.

A Boy and His Atom is a 2012 stop-motion animated short film released by IBM Research. The movie tells the story of a boy and a wayward atom who meet and become friends. It depicts a boy playing with an atom that takes various forms. It was made by moving carbon monoxide molecules viewed with a scanning tunneling microscope, a device that magnifies them 100 million times. These molecules were moved to create images, which were then saved as individual frames to make the film.

## Key Takeaways

- Chemistry is based on the modern atomic theory, which states that all matter is composed of atoms.
- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.

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# 2.4: Elements and Atomic Number

**Learning Objectives**

- Define the atomic and mass numbers.
- Identify the number of protons and neutrons in an atom.
- Write or interpret the AXZ notation for an atom.

## Atomic Number

The modern atomic theory states that atoms of one element are the same, while atoms of different elements are different. What makes atoms of different elements different? The fundamental characteristic that all atoms of the same element share is the *number of protons*. All atoms of hydrogen have one and only one proton in the nucleus; all atoms of iron have 26 protons in the nucleus. This number of protons is so important to the identity of an atom that it is called the **atomic number (*Z*).** The number of protons in an atom is the atomic number of the element. Thus, hydrogen has an atomic number of 1, while iron has an atomic number of 26. Each element has its own characteristic atomic number.

Atoms are electrically *neutral*, meaning that the overall electric charge is zero. This is because the number of protons (positive charge) equals the number of electrons (negative charge). Therefore, the atomic number also provides the number of electrons. For example, helium has $Z = 2$, which tells us that there are 2 protons in the nucleus and 2 electrons outside of the nucleus. Sometimes atoms will gain or lose electrons resulting in a difference in the number of protons and electrons, which means the charge is no longer zero. Atoms that have a charge are called *ions* and will be discussed further in the next chapter.

## Mass Number

As we learned in the previous section, protons and neutrons, which are found in the nucleus of an atom, each have a mass of ~1 amu. Because an electron has negligible mass relative to that of a proton or a neutron, the majority of an atom's mass is in the nucleus. The **mass number (*A*)** is defined as the total number of protons ($p^+$) and neutrons ($n$) in an atom:

$$A = p^+ + n \tag{2.4.1}$$

Atoms of the same element always have the same number of protons, same *Z*, but often have different numbers of neutrons, therefore, different mass numbers. These atoms are called **isotopes** and are introduced in next section.

**2.4.1 Example**

a. The most common carbon atoms have six protons and six neutrons in their nuclei. What are the atomic number and the mass number of these carbon atoms?
b. An isotope of uranium has an atomic number of 92 and a mass number of 235. What are the number of protons and neutrons in the nucleus of this atom?

**Solution**

a. If a carbon atom has six protons in its nucleus, its atomic number is 6. If it also has six neutrons in the nucleus, then the mass number is 6 + 6, or 12.
b. If the atomic number of uranium is 92, then that is the number of protons in the nucleus. Because the mass number is 235, then the number of neutrons in the nucleus is 235 − 92, or 143.

**2.4.1 Exercise**

The number of protons in the nucleus of a tin atom is 50, while the number of neutrons in the nucleus is 68. What are the atomic number and the mass number of this isotope?

**Answer**

Atomic number = 50, mass number = 118

## Symbolic Representations - AXZ Notation

A simple way of indicating the mass number of a particular atom is to list it as a superscript on the left side of an element's symbol. Atomic numbers are often listed as a subscript on the left side of an element's symbol (Figure 2.4.1).

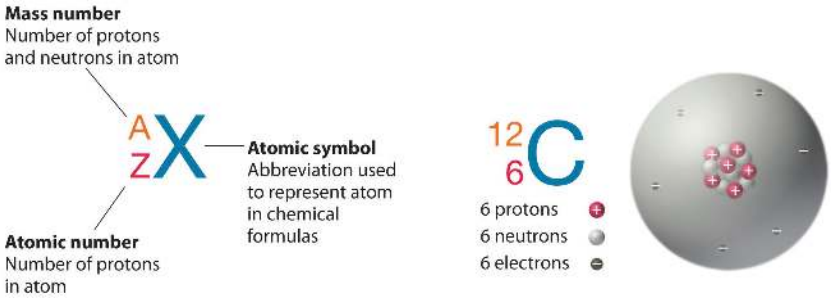



Figure 2.4.1: Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons and electrons, 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. (CC BY-NC-SA 4.0; anonymous by request)

Figure 2.4.1 shows an easy way to represent isotopes using the atomic symbols where $X$ is the symbol of the element, $A$ is the mass number, and $Z$ is the atomic number. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is

$$^{12}_{6}\mathrm{C}$$

where $C$ is the symbol for the element, 6 represents the atomic number, and 12 represents the mass number.

It is also common to state the mass number after the name of an element to indicate a particular isotope. *Carbon-12* represents an isotope of carbon with 6 protons and 6 neutrons, while *uranium-238* is an isotope of uranium that has 146 neutrons.

### 2.4.2Example :

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?
b. How many protons and neutrons are in $^{56}_{26}\mathrm{Fe}$

**Solution**

a. The symbol for this isotope is $^{235}_{92}\mathrm{U}$
b. This iron atom has 26 protons and 56 − 26 = 30 neutrons.

### 2.4.2Exercise

How many protons are in $^{23}_{11}\mathrm{Na}$

**Answer**

11 protons

## Key Takeaways

- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.
- Isotopes of an element contain different numbers of neutrons.
- Elements are represented by an atomic symbol.

## Contributors

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# 2.5: Isotopes and Atomic Weight

**Learning Objectives**

- Explain how isotopes differ from one another.
- Calculate the atomic mass of an element from the masses and relative percentages of the isotopes of the element.

## Isotopes

As introduced previously, atoms of a specific element are distinguished from other elements by their atomic number, (the number of protons). Atoms of the same element always have the same number of protons, however, the number of neutrons can vary. **Isotopes** are atoms of the same element that contain *different* numbers of *neutrons*. This difference in neutron amount affects the mass number (*A*) but not the atomic number (*Z*). In a chemical laboratory, isotopes of an element appear and react the same. For this reason, it is difficult to distinguish between different isotopes. In contrast, nuclear scientists can identify and separate different types of atomic nuclei. The technology required for this process is more sophisticated that what could be found in a typical chemical laboratory.

Figure **2.5.1** shows an easy way to represent isotopes with a **nuclear symbol**, which includes the atomic or element symbol (represented by $X$), the mass number, $A$, and the atomic number, $Z$. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is:

$$^{12}_{6}\mathrm{C}$$

where $C$ is the symbol for carbon, 6 represents the atomic number, and 12 represents the mass number.

It is also common to state the mass number after the name of an element to indicate a particular isotope. *Carbon-12* represents an isotope of carbon with 6 protons and 6 neutrons, while *uranium-238* is an isotope of uranium that has 92 protons and 146 neutrons.

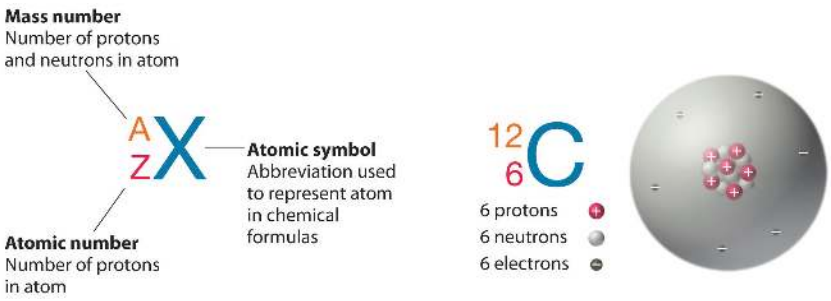



Figure **2.5.1**: Nuclear Symbol. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons 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. (CC BY-NC-SA 4.0; anonymous by request)

Most elements on the periodic table have at least two stable isotopes. For example, in addition to $^{12}\mathrm{C}$, a typical sample of carbon contains 1.11% $^{13}_{6}\mathrm{C}$, with 7 neutrons and 6 protons, and a trace of $^{14}_{6}\mathrm{C}$, with 8 neutrons and 6 protons. The nucleus of $^{14}_{6}\mathrm{C}$ 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. There are about twenty elements that exist in only one isotopic form (sodium and fluorine are examples of these).

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure **2.5.2** compares the three isotopes of hydrogen.

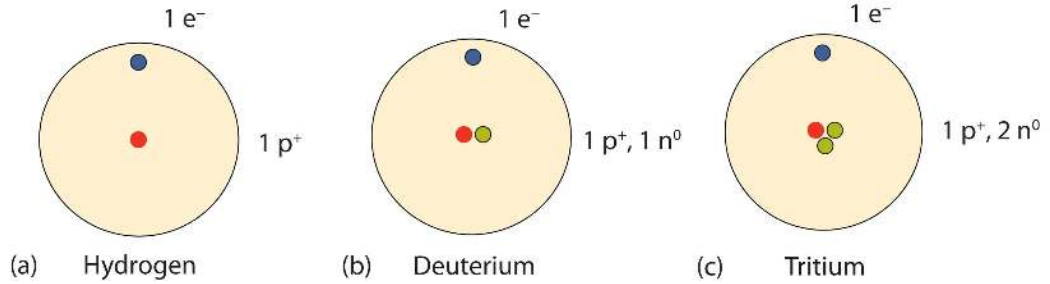



Figure **2.5.2**: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

There are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. A/Z and symbol-mass formats can be used to display periodic table information. When viewing either of these two notations, isotopic differences can be obtained.

> *The discovery of isotopes required a minor change in Dalton's atomic theory. Dalton thought that all atoms of the same element were exactly the same.*

Look at the **A/Z formats** for the three isotopes of hydrogen in Table **2.5.1**. Note how the atomic number (bottom value) remains the same while the atomic masses (top number) are varied. All isotopes of a particular element will vary in neutrons and mass. This variance in mass will be visible in the **symbol-mass format** of same isotopes as well.

Table **2.5.1**

| Common Name | A/Z formats | symbol-mass format | Expanded Name |
|---|---|---|---|
| Hydrogen | $^{1}_{1}\mathbf{H}$ | **H-1** | hydrogen-1 |
| Deuterium | $^{2}_{1}\mathbf{H}$ | **H-2** | hydrogen-2 |
| Tritium | $^{3}_{1}\mathbf{H}$ | **H-3** | hydrogen-3 |

Both A/Z or symbol-mass formats can be utilized to determine the amount of subatomic particles (protons, neutrons, and electrons) contained inside an isotope. When given either format, these mass values should be used to calculate the number of neutrons in the nucleus.

## Atomic Weight

Since most naturally occurring elements samples are mixtures of isotopes, it is useful to use an average weight of an element. The **atomic mass** of an element is the weighted mass of all the naturally presented isotopes (on earth). To determine the most abundant isotopic form of an element, compare given isotopes to the weighted average on the periodic table. For example, the three hydrogen isotopes in Figure **2.5.2** are H-1, H-2, and H-3. The atomic mass or weighted average of hydrogen is around 1.008 amu ( look again to the periodic table). Of the three hydrogen isotopes, H-1 is closest in mass to the weighted average; therefore, it is the most abundant. The other two isotopes of hydrogen are quite rare, but are very exciting in the world of nuclear science.

You can calculate the atomic mass (or average mass) of an element provided you know the **relative abundances** (the fraction of an element that is a given isotope), the element's naturally occurring isotopes, and the masses of those different isotopes. We can calculate this by the following equation:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots \tag{2.5.1}$$

Averages like Equation 1 are known as *weighted averages*. An element's atomic mass can be calculated provided the relative abundances of the element's naturally occurring isotopes and the masses of those isotopes are known. If all the abundances are not provided, it is safe to assume that all numbers should add up to 100%.

For example, Boron has two naturally occurring isotopes. In a sample of boron, 20% of the atoms are B-10, which is an isotope of boron with 5 neutrons and mass of 10 amu. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of 11 amu. How do we calculate the atomic mass of boron?

Boron has two isotopes so we will use the Equation 2.5.1 and substitute the relative abundances and atomic masses of Boron into Equation 2.5.1:

$$\begin{aligned}\text{Atomic mass} &= (0.20)\,(10) + (0.80)\,(11)\\ &= 10.8\ \text{amu}\end{aligned}$$

The mass of an average boron atom, and thus boron's atomic mass, is 10.8 amu.

### Example 2.5.1: Atomic Weight of Neon

Neon has three naturally occurring isotopes. In a sample of neon, 90.92% of the atoms are Ne-20, which is an isotope of neon with 10 neutrons and a mass of 19.99 amu. Another 0.3% of the atoms are Ne-21, which is an isotope of neon with 11 neutrons and a mass of 20.99 amu. The final 8.85% of the atoms are Ne-22, which is an isotope of neon with 12 neutrons and a mass of 21.99 amu. What is the atomic mass of neon?

#### Solution

Neon has three isotopes. We will use the equation:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots$$

Substitute these into the equation, and we get:

$$\begin{aligned}\text{Atomic mass} &= (0.9092)\,(19.99) + (0.003)\,(20.99) + (0.0885)\,(21.99)\\ &= 20.17\ \text{amu}\end{aligned}$$

The mass of an average neon atom is 20.17 amu

### Exercise 2.5.1

Magnesium has the three isotopes listed in the following table:

Table showing the 3 isotopes of magnesium, the exact mass of each, and the percent abundance of each.

| 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

### Applications of Isotopes

During the Manhattan project, the majority of federal funding was dedicated the separation of uranium isotopes. The two most common isotopes of uranium are U-238 and U-235. About 99.3% of uranium is of the U-238 variety, this form is not fissionable and will not work in a nuclear weapon or reaction. The remaining 0.7% is U-235 which is fissionable, but first had to be separated from U-238. This separation process is called *enrichment*. During World War II, a nuclear facility was built in Oak Ridge, Tennessee to accomplish this project. At the time, the enrichment process only produced enough U-235 for one nuclear weapon. This fuel was placed inside the smaller of the two atomic bombs (Little Boy) dropped over Japan.




Figure **2.5.3**: A billet of highly enriched uranium that was recovered from scrap processed at the Y-12 National Security Complex Plant. Original and unrotated.

A billet of highly enriched uranium that was recovered from scrap processed at the Y-12 National Security Complex Plant.

Uranium is a natural element that can be found in several different countries. Countries that do not have natural uranium supplies would need to obtain it from one of the countries below. Most nuclear reactors that provide energy rely on U-235 as a source of fuel. Fortunately, reactors only need 2-5% U-235 for the production of megawatts or even gigawatts of power. If the purification process exceeds this level, than it is likely a country is focusing on making nuclear weapons. For example, Manhattan Project scientists enriched U-235 up to 90% in order to produce the Little Boy weapon.

Abbreviations like HEU (highly enriched uranium) and LEU (low-enriched uranium) are used frequently by nuclear scientists and groups. HEU is defined as being over 20% pure U-235 and would not be used in most commercial nuclear reactors. This type of material is used to fuel larger submarines and aircraft carriers. If the purification of U-235 reaches 90%, then the HEU is further classified as being weapons grade material. This type of U-235 could be used to make a nuclear weapon (fission or even fusion based). As for LEU, its U-235 level would be below this 20% mark. LEU would be used for commercial nuclear reactors and smaller, nuclear powered submarines. LEU is not pure enough to be used in a conventional nuclear weapon, but could be used in a dirty bomb. This type of weapon uses conventional explosives like dynamite to spread nuclear material. Unlike a nuclear weapon, dirty bombs are not powerful enough to affect large groups of buildings or people. Unfortunately, the spread of nuclear material would cause massive chaos for a community and would result in casualties.

## Summary

- The isotopes of an element have different masses and are identified by their mass numbers.
- An element's atomic mass is the weighted average of the masses of the isotopes of an element
- An element's atomic mass can be calculated provided the relative abundances of the element's naturally occurring isotopes and the masses of those isotopes are known. If all the abundances are not provided, it is safe to assume that all numbers should add up to 100%.

## Concept Review Exercises

1. Why is the atomic number so important to the identity of an atom?
2. What is the relationship between the number of protons and the number of electrons in an atom?
3. How do isotopes of an element differ from each other?
4. What is the mass number of an element?

## Answers

1. The atomic number defines the identity of an element. It describes the number of protons in the nucleus.
2. In an electrically neutral atom, the number of protons equals the number of electrons.
3. Isotopes of an element have the same number of protons but have different numbers of neutrons in their nuclei.
4. The mass number is the sum of the numbers of protons and neutrons in the nucleus of an atom.

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- Elizabeth R. Gordon (Furman University)

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# 2.6: The Quantum-Mechanical Model- Atoms with Orbitals

**Learning Objectives**

- Define quantum mechanics
- Differentiate between an orbit and an orbital.
- Recognize the structure of shells and subshells in an atom.

Although we have discussed the general arrangement of subatomic particles in atoms, we have said little about how electrons occupy the space about the nucleus. Do they move around the nucleus at random, or do they exist in some ordered arrangement? The current model for describing the position of electrons in an atom is called the quantum mechanical model.

## Quantum Mechanics

The study of motion of large objects such as baseballs is called mechanics, or more specifically, classical mechanics. Because of the quantum nature of the electron and other tiny particles moving at high speeds, classical mechanics is inadequate to accurately describe their motion. **Quantum mechanics** is the study of the motion of objects that are atomic or subatomic in size and thus demonstrate wave-particle duality. In classical mechanics, the size and mass of the objects involved effectively obscures any quantum effects, so that such objects appear to gain or lose energies in any amounts. Particles whose motion is described by quantum mechanics gain or lose energy in small pieces called **quanta**.

One of the fundamental (and hardest to understand) principles of quantum mechanics is that the electron is both a particle and a wave. In the everyday macroscopic world of things we can see, something cannot be both. But this duality can exist in the quantum world of the submicroscopic on the atomic scale.

At the heart of quantum mechanics is the idea that we cannot accurately specify the location of an electron. All we can say is that there is a probability that it exists within this certain volume of space. The scientist Erwin Schrödinger developed an equation that deals with these calculations, which we will not pursue at this time.



*Erwin Schrödinger.*

## Atomic Orbitals

In an atom, electrons exist in regions of space called orbitals. Quantum mechanics defines an orbital as a region of space around the nucleus where an electron has a high probability of existing, and **one orbital can hold up to two electrons.**

There are several types of orbitals that have a specific shape and energy. Although there are many theoretical options, the atoms we encounter have electrons in 4 types of orbitals - s, p, d and f. Here are the shapes of s and p orbitals, which represent the region where we are most likely to find an electron.

### s Orbitals

The s orbital has a  spherical shape:

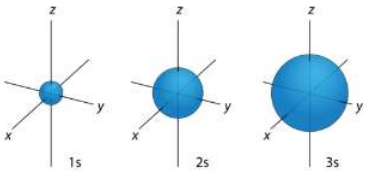



Figure **2.6.2**: ***s*** orbitals have no orientational preference and resemble spheres.

### p Orbitals

For p orbitals, there are three types of orbitals that have different orientations in the atom.

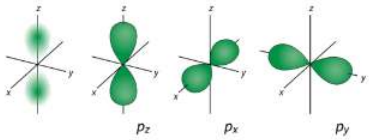



Figure **2.6.3**: ***p*** orbitals have an orientational preference and resemble dumbbells.

## General Organization of Orbitals in the Atom

The orbitals in an atom are organized according to their energy. Within the quantum model,

- Electrons in atoms can have only certain specific energies. We say that the energies of the electrons are quantized.
- Electrons are organized according to their energies into sets called **shells** (labeled by the principle quantum number, ***n***). Generally the higher the energy of a shell, the farther it is (on average) from the nucleus. Shells do not have specific, fixed distances from the nucleus, but an electron in a higher-energy shell will spend more time farther from the nucleus than does an electron in a lower-energy shell.
- Shells are further divided into subsets of electrons called **subshells**. The first shell has only one subshell, the second shell has two subshells, the third shell has three subshells, and so on. The subshells of each shell are labeled, in order, with the letters *s*, *p*, *d*, and *f*. Thus, the first shell has only a single *s* subshell (called **1*s***), the second shell has **2*s*** and **2*p*** subshells, the third shell has **3*s***, **3*p***, and **3*d*** and so forth.

Table **2.6.1**: Shells and Subshells

| Shell | Number of Subshells | Names of Subshells |
|---|---|---|
| 1 | 1 | *1s* |
| 2 | 2 | *2s* and *2p* |
| 3 | 3 | *3s*, *3p* and *3d* |
| 4 | 4 | *4s*, *4p*, *4d* and *4f* |

- Different subshells hold a different maximum number of electrons. **Any *s* subshell can hold up to 2 electrons; *p*, 6; *d*, 10; and *f*, 14.**

Table **2.6.2**: Number of Electrons

| Subshell | Maximum Number of Electrons |
|---|---|
| *s* | 2 |
| *p* | 6 |
| *d* | 10 |
| *f* | 14 |

It is the arrangement of electrons into shells and subshells that most concerns us here, and we will focus on that in the next section.

## Summary

Quantum mechanics involves the study of material at the atomic level. This field deals with probabilities, since we cannot definitely locate a particle. Orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

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# 2.7: Electron Configurations

## Learning Objectives

- Describe how electrons are grouped within atoms.
- Write electron configurations for atoms.
- Connect the electron configuration of atoms to the energy levels of the electrons in the atom.

Previously we discussed the concept of electron shells and subshells. It is the arrangement of electrons into shells and subshells that most concerns us here, so we will focus on that.

## General Rules of Electron Configuration

There are a set of general rules that are used to figure out the electron configuration of an atomic species: **Aufbau Principle**, **Hund's Rule** and the **Pauli-Exclusion Principle**. Before continuing, it's important to understand that each orbital can be occupied by *two* electrons.

- Rule 1 (Aufbau Principle): Electrons occupy the lowest-energy orbitals possible, starting with 1s and continuing in the order dictated by quantum mechanics
- Rule 2 (Hund's Rule): Electrons occupy degenerate orbitals (i.e. same $n$ and $\ell$ quantum numbers), they must first occupy the empty orbitals before double occupying them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all same $m_s$ quantum numbers).
- Rule 3 (Pauli-Exclusion Principle): Each electron can be described with a unique set of four quantum numbers. Therefore, if two electrons occupy the same orbital, they have different spin - spin up or spin down.

## Electron Configurations

Electron configurations are are shorthand descriptions of the arrangements of electrons in atoms. An example electron configuration with its general structure is shown in Figure **2.7.1**. In electron configurations, we use numbers to indicate which shell an electron is in.

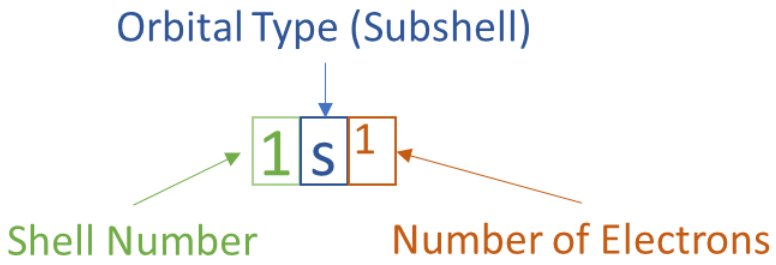



Figure **2.7.1**: General structure of electron configurations.

As shown in Table **2.7.1**, the first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1*s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $\mathbf{1}s^{\mathbf{1}}$ to describe the electronic structure of hydrogen.

Table **2.7.1**: Shells and Subshells

| Shell | Number of Subshells | Names of Subshells |
|---|---|---|
| 1 | 1 | *1s* |
| 2 | 2 | *2s* and *2p* |
| 3 | 3 | *3s*, *3p* and *3d* |
| 4 | 4 | *4s*, *4p*, *4d* and *4f* |

Helium atoms have 2 electrons. Both electrons fit into the 1*s* subshell because *s* subshells can hold up to 2 electrons; therefore, the electron configuration for helium atoms is $\mathbf{1}s^2$ (spoken as "one-ess-two"). Different subshells hold a different maximum number of electrons. Any s subshell can hold up to 2 electrons; p, 6; d, 10; and f, 14 (Table **2.7.2**). Hence, the 1*s* subshell cannot hold 3 electrons (because an *s* subshell can hold a maximum of 2 electrons), so the electron configuration for a lithium atom cannot be $1s^3$ (Figure **2.7.2**). Two of the lithium electrons can fit into the 1*s* subshell, but the third electron must go into the second shell. The second shell has two subshells, *s* and *p*, which fill with electrons in that order. The 2*s* subshell holds a maximum of 2 electrons, and the 2*p* subshell holds a maximum of 6 electrons. Because lithium's final electron goes into the 2*s* subshell, we write the electron configuration of a lithium atom as $\mathbf{1}s^2\mathbf{2}s^1$**.** The shell diagram for a lithium atom (Figure **2.7.1**). The shell closest to the nucleus (first shell) has 2 dots representing the 2 electrons in **1s**, while the outermost shell (**2s**) has 1 electron.

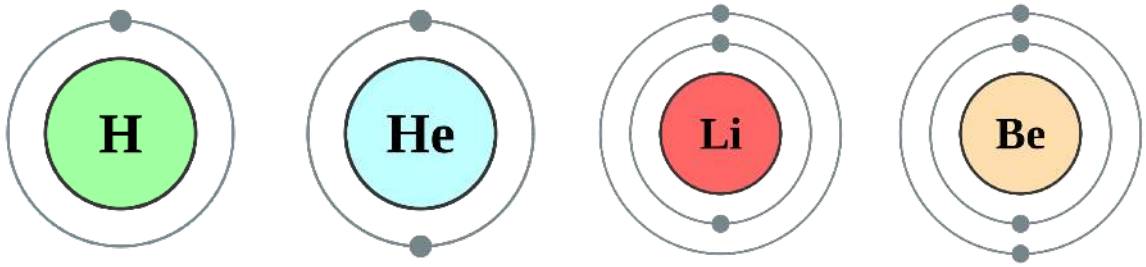



Figure **2.7.2**: Shell diagrams of hydrogen (H), helium (He), lithium (Li), and Berryellium (Be) atoms. (CC BY-SA 2.0 UK; Greg Robson modified by Pumbaa via Wikipedia)

Table **2.7.2**: Number of Electrons in subshells

| Subshell | Maximum Number of Electrons |
|---|---|
| *s* | 2 |
| *p* | 6 |
| *d* | 10 |
| *f* | 14 |

The next largest atom, beryllium, has 4 electrons, so its electron configuration is $1s^22s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms start filling the 2*p* subshell. With neon, the 2*p* subshell is completely filled. Because the second shell has only two subshells, atoms with more electrons now must begin the third shell. The third shell has three subshells, labeled *s*, *p*, and *d*. The *d* subshell can hold a maximum of 10 electrons. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^22s^22p^63s^23p^1$. However, a curious thing happens after the 3*p* subshell is filled: the 4*s* subshell begins to fill before the 3*d* subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms. A fourth subshell, the *f* subshell, is needed to complete the electron configurations for all elements. An *f* subshell can hold up to 14 electrons.

Table **2.7.3**: Atomic Electron Configurations

| Z | Element | Outer most Shell | Configuration | Noble Gas Configuration |
|---|---|---|---|---|
| 1 | H | 1 | $1s^1$ | $1s^1$ |
| 2 | He | 1 | $1s^2$ | $1s^2$ |
| 3 | Li | 2 | $1s^2 2s^1$ | [He] $2s^1$ |
| 4 | Be | 2 | $1s^2 2s^2$ | [He] $2s^2$ |
| 5 | B | 2 | $1s^2 2s^2 2p^1$ | [He] $2s^2 2p^1$ |
| 6 | C | 2 | $1s^2 2s^2 2p^2$ | [He] $2s^2 2p^2$ |
| 7 | N | 2 | $1s^2 2s^2 2p^3$ | [He] $2s^2 2p^3$ |
| 8 | O | 2 | $1s^2 2s^2 2p^4$ | [He] $2s^2 2p^4$ |
| 9 | F | 2 | $1s^2 2s^2 2p^5$ | [He] $2s^2 2p^5$ |
| 10 | Ne | 2 | $1s^2 2s^2 2p^6$ | [He] $2s^2 2p^6$ |
| 11 | Na | 3 | $1s^2 2s^2 2p^6 3s^1$ | [Ne] $3s^1$ |
| 12 | Mg | 3 | $1s^2 2s^2 2p^6 3s^2$ | [Ne] $3s^2$ |
| 13 | Al | 3 | $1s^2 2s^2 2p^6 3s^2 3p^1$ | [Ne] $3s^2 3p^1$ |
| 14 | Si | 3 | $1s^2 2s^2 2p^6 3s^2 3p^2$ | [Ne]$3s^2 3p^2$ |
| 15 | P | 3 | $1s^2 2s^2 2p^6 3s^2 3p^3$ | [Ne] $3s^2 3p^3$ |
| 16 | S | 3 | $1s^2 2s^2 2p^6 3s^2 3p^4$ | [Ne] $3s^2 3p^4$ |
| 17 | Cl | 3 | $1s^2 2s^2 2p^6 3s^2 3p^5$ | [Ne] $3s^2 3p^5$ |
| 18 | Ar | 3 | $1s^2 2s^2 2p^6 3s^2 3p^6$ | [Ne] $3s^2 3p^6$ |
| 19 | K | 4 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ | [Ar] $4s^1$ |
| 20 | Ca | 4 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ | [Ar] $4s^2$ |

Electron filling always starts with **1*s***, the subshell closest to the nucleus. Next is **2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5s, 4d, 5p, 6s,** etc., shown in the electron shell filling order diagram in Figure **2.7.3**. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

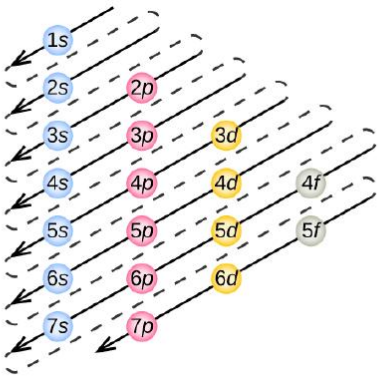



Figure **2.7.3**: The order of electron filling in an atom.

## Noble Gas Configuration

The electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$ (Table 2.7.3). The first ten electrons of the sodium atom are the inner-shell electrons and the configuration of just those ten electrons is exactly the same as the configuration of the element neon ($Z = 10$). This provides the basis for a shorthand notation for electron configurations called the **noble gas configuration**, which atom consists of the elemental symbol of the last noble gas prior to that atom, followed by the configuration of the remaining electrons. So for sodium, we make the substitution of [Ne] for the $1s^2 2s^2 2p^6$ part of the configuration. Sodium's noble gas configuration becomes $[Ne]\,3s^1$. Table 2.7.1 shows the noble gas configurations of the third period elements.

## Electron Configurations and Orbital Diagrams

We construct the periodic table by following the aufbau principle (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 2.7.1, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_s = +½$, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_s = −½$. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

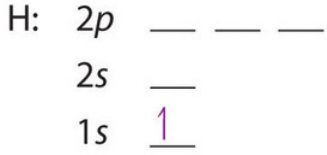
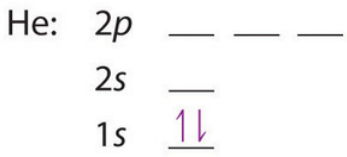



Figure 2.7.1: One electron in.

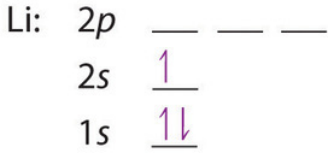
From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number *n* and their value of *l* (*s*, *p*, *d*, or *f*), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy (Figure 2.7.1), and the electron configuration is written as $1s^1$ and read as "one-s-one."

A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1*s* orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



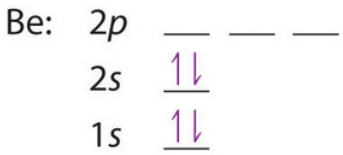

written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1*s* orbital can hold two of the electrons with their spins paired; the third electron must enter a higher energy orbital. Figure 6.29 tells us that the next lowest energy orbital is 2*s*, so the orbital diagram for lithium is

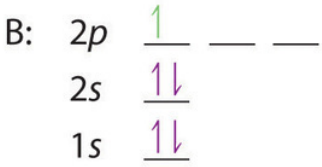



This electron configuration is written as $1s^2 2s^1$.

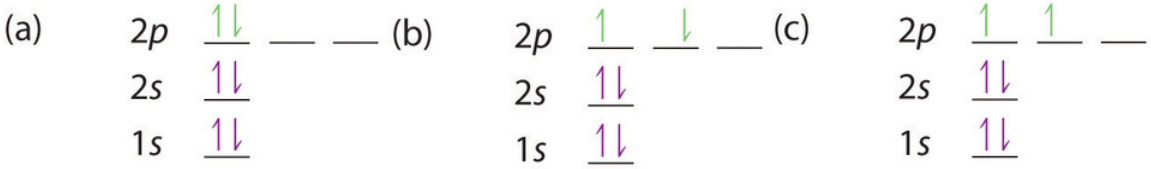
The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1*s* and 2*s* orbitals to achieve a $1s^2 2s^2$ electron configuration:




When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:

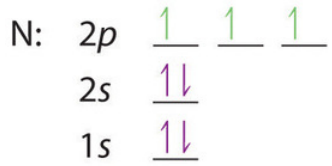



At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?



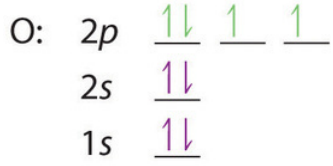

Because of electron-electron interactions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates **Hund's rule** (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

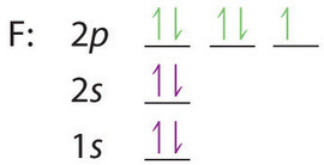



with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

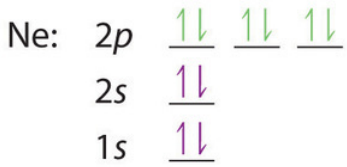
At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the 2*p* orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the 2*p* orbitals are degenerate, it doesn't matter which one has the pair of electrons.




Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:




When we reach neon, with $Z = 10$, we have filled the 2*p* subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:




Notice that for neon, as for helium, all the orbitals through the 2*p* level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

### 2.7.1 Example : Electronic Configuration of Phosphorus Atoms

Using Figure **2.7.2** as your guide, write the electron configuration of a neutral phosphorus atom. The atomic number of P is 15.

**Solution**

A neutral phosphorus atom has 15 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 5 electrons. Of those 5 electrons, 2 can go into the 3*s* subshell, and the remaining 3 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral phosphorus atoms is $1s^2 2s^2 2p^6 3s^2 3p^3$.

### 2.7.1 Exercise : Electronic Configuration of Chlorine Atoms

Using Figure **2.7.2** as your guide, write the electron configuration of a neutral chlorine atom. The atomic number of Cl is 17.

**Answer**

A neutral chlorine atom has 17 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 7 electrons. Of those 7 electrons, 2 can go into the 3*s* subshell, and the remaining 5 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral chlorine atoms is $1s^2 2s^2 2p^6 3s^2 3p^5$.

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# 2.8: Electron Configurations and the Periodic Table

**Learning Objectives**

- Relate the electron configurations of the elements to the shape of the periodic table.
- Determine the expected electron configuration of an element by its place on the periodic table.

Previously, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure **2.8.1**. The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.

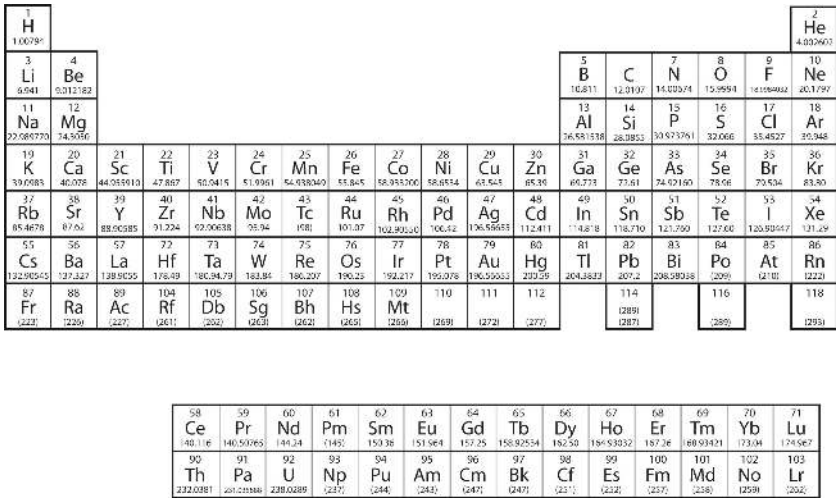



Figure **2.8.1**: The Periodic Table

Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations: the shape of the periodic table mimics the filling of the subshells with electrons.

> *The shape of the periodic table mimics the filling of the subshells with electrons.*

## Electron Configurations and the Periodic Table

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the $n = 1$ shell is filled. These two elements make up the first row of the periodic table (Figure **2.8.2**)

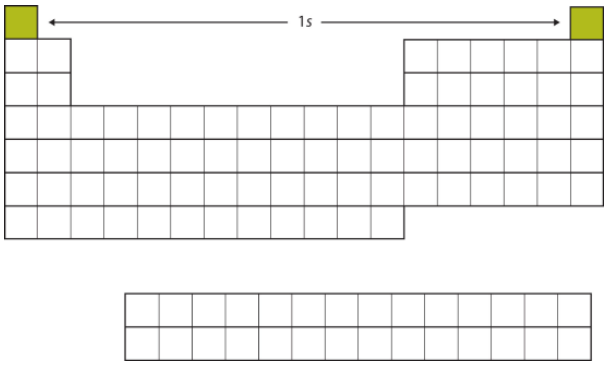



Figure **2.8.2**: The 1*s* Subshell. H and He represent the filling of the 1*s* subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure **2.8.3** shows that these two elements are adjacent on the periodic table.

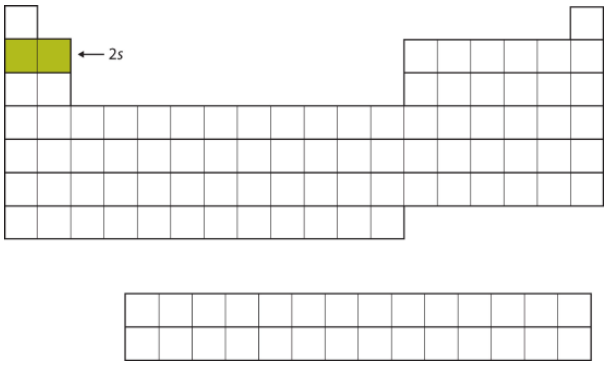



Figure 2.8.3: The 2*s* Subshell. In Li and Be, the 2*s* subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 2.8.4).

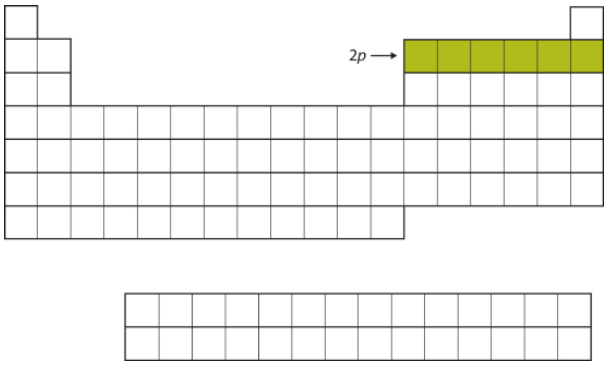



Figure 2.8.4: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 2.8.5).

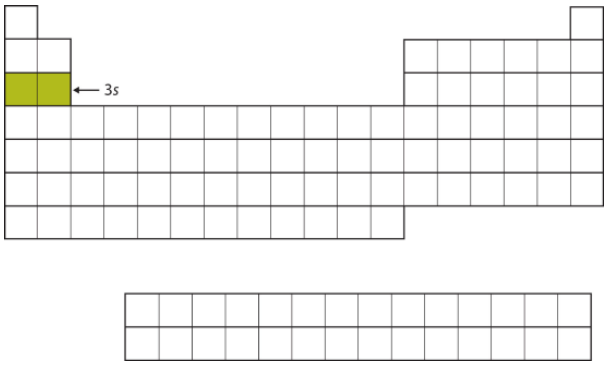



Figure 2.8.5: The 3*s* Subshell. Now the 3*s* subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 2.8.6).

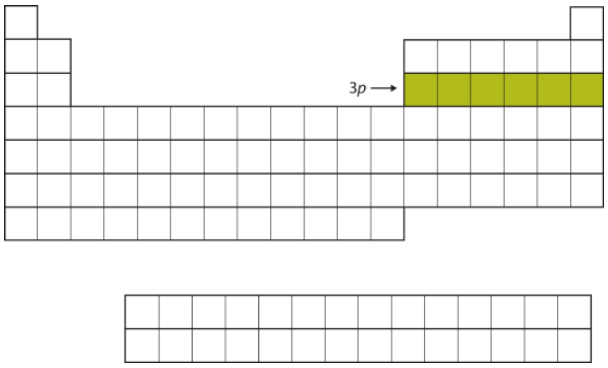



Figure **2.8.6**: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure **2.8.7**).

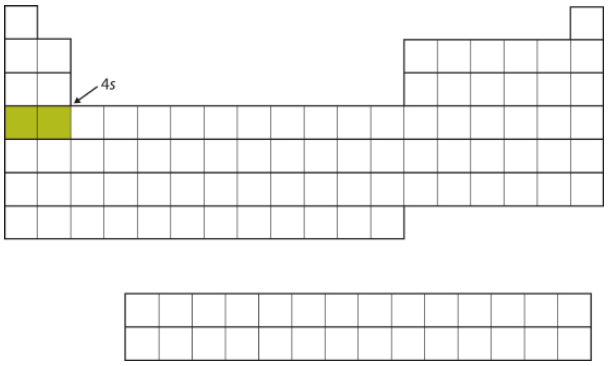



Figure **2.8.7**: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure **2.8.8**).

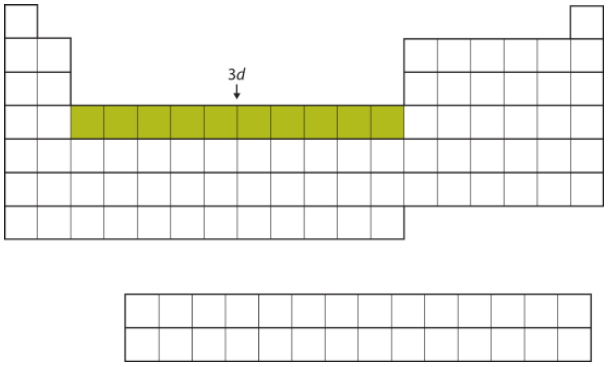



Figure **2.8.8**: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

...And so forth. As we go across the rows of the periodic table, the overall shape of the table outlines how the electrons are occupying the shells and subshells.

## The Blocks of the Periodic Table

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** are the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure **2.8.9** shows the blocks of the periodic table.

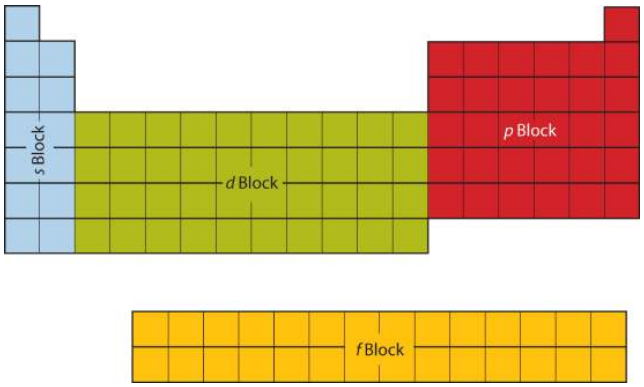



Figure **2.8.9**: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

| | |
|---|---|
| H: | $1s^{\mathbf{1}}$ |
| Li: | $1s^2\mathbf{2s^1}$ |
| Na: | $[Ne]\mathbf{3s^1}$ |
| K: | $[Ar]\mathbf{4s^1}$ |
| Rb: | $[Kr]\mathbf{5s^1}$ |
| Cs: | $[Xe]\mathbf{6s^1}$ |

They all have a similar electron configuration in their valence shells: a single *s* electron. Because much of the chemistry of an element is influenced by valence electrons, we would expect that these elements would have similar chemistry—*and they do*. The organization of electrons in atoms explains not only the shape of the periodic table, but also the fact that elements in the same column of the periodic table have similar chemistry.

The same concept applies to the other columns of the periodic table. Elements in each column have the same valence shell electron configurations, and the elements have some similar chemical properties. This is strictly true for all elements in the *s* and *p* blocks. In the *d* and *f* blocks, because there are exceptions to the order of filling of subshells with electrons, similar valence shells are not absolute in these blocks. However, many similarities do exist in these blocks, so a similarity in chemical properties is expected.

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure **2.8.10**. It is in the fourth column of the *p* block. This means that its electron configuration should end in a $p^4$ electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^23d^{10}4p^4$, as expected.

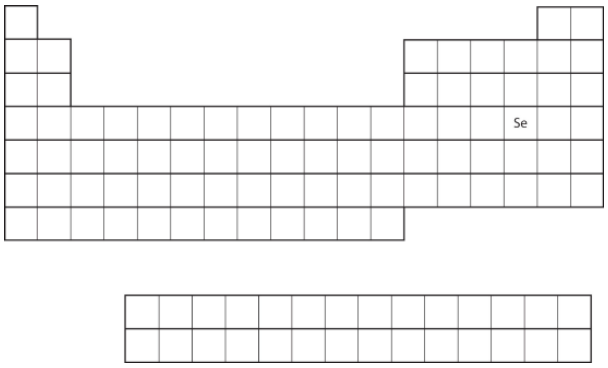



Figure **2.8.10**: Selenium on the Periodic Table

## Example 2.8.1: Predicting Electron Configurations

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure **2.8.11**).

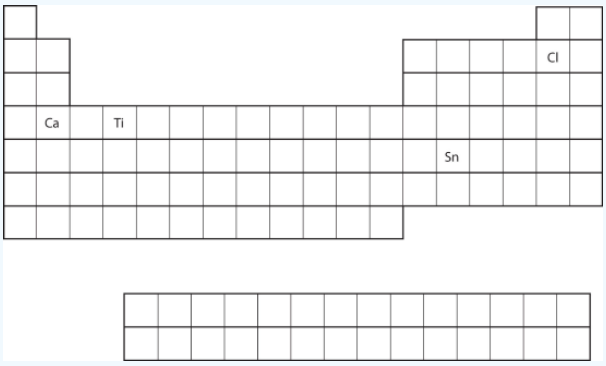



Figure **2.8.11**: Various Elements on the Periodic Table

a. Ca
b. Sn

### Solution

a. Ca is located in the second column of the *s* block. We expect that its electron configuration should end with $s^2$. Calcium's electron configuration is $[Ar]4s^2$.
b. Sn is located in the second column of the *p* block, so we expect that its electron configuration would end in $p^2$. Tin's electron configuration is $[Kr]5s^24d^{10}5p^2$.

## Exercise 2.8.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure **2.8.11**.

a. Ti
b. Cl

**Answer a**

$[Ar]4s^23d^2$

**Answer b**

$[Ne]3s^23p^5$


https://chem.libretexts.org/@go/page/393858

## Summary

The arrangement of electrons in atoms is responsible for the shape of the periodic table. Electron configurations can be predicted by the position of an atom on the periodic table.

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# 2.9: Valence Electrons

**Learning Objectives**

- Identify valence electrons using the periodic table and electron configuration.
- Define core and valence electrons.

## Valence Electrons

In the study of chemical reactivity, we will find that the electrons in the outermost principal energy level are very important and so they are given a special name. **Valence electrons** are the electrons in the highest occupied principal energy level of an atom.

In the second period elements, the two electrons in the $\mathbf{1}s$ sublevel are called **inner-shell electrons** and are not involved directly in the element's reactivity or in the formation of compounds. Lithium has a single electron in the second principal energy level and so we say that lithium has one valence electron. Beryllium has two valence electrons. How many valence electrons does boron have? You must recognize that the second principal energy level consists of both the $\mathbf{2}s$ and the $\mathbf{2}p$ sublevels and so the answer is three. In fact, the number of valence electrons goes up by one for each step across a period until the last element is reached. Neon, with its configuration ending in $\mathbf{2}s^{\mathbf{2}}\mathbf{2}p^{\mathbf{6}}$, has eight valence electrons.

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 $1s^22s^22p^63s^1$ 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 \PageIndex4). 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, ($1s^22s^22p^6$) and our abbreviated or condensed configuration is $[Ne]3s^1$.

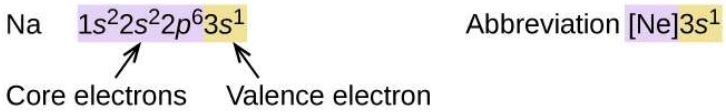



Figure **2.9.1**: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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.

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

A chemical reaction results from electron removal, electron addition, or electron sharing of the valence electrons of the different atoms. The path a specific element will take depends on where the electrons are in the atom and how many there are. Thus, it is convenient to separate electrons into two groups. Valence shell electrons (or, more simply, the *valence electrons*) are the electrons in the highest-numbered shell, or valence shell, while core electrons are the electrons in lower-numbered shells. We can see from the electron configuration of a carbon atom—$1s^22s^22p^2$—that it has 4 valence electrons ($2s^22p^2$) and 2 core electrons ($1s^2$). You will see in the next chapters that the chemical properties of elements are determined by the number of valence electrons.

**Example 2.9.3**

Examine the electron configuration of neutral phosphorus atoms in Example **2.9.1**, $1s^22s^22p^63s^23p^3$ and write the abbreviated notation.

**Solution**

Phosphorus has electron configuration, $1s^22s^22p^63s^23p^3$.

The highest-numbered shell is the third shell ($3s^2 3p^3$): **2 electrons** in the 3*s* subshell and **3 electrons** in the 3*p* subshell. That gives a total of **5 valence electrons**.

The 10 inner shell (core) electrons, $1s^2 2s^2 2p^6$ can be replaced by [Ne] (see Figure **2.9.3**). Abbreviated notation is : $[Ne]3s^2 3p^3$

## ? Exercise 2.9.3

Examine the electron configuration of neutral calcium atom (Exercise **2.9.2**), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, and write the abbreviated notation.

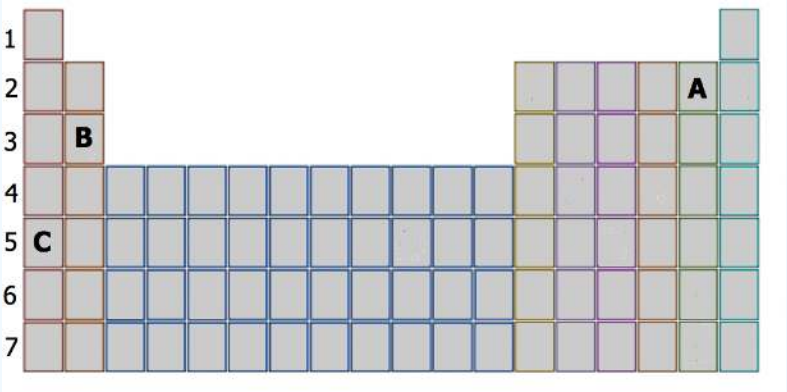
**Answer**

The highest-numbered shell is the fourth shell $4s^2$, which has **2 electrons** in the *4s* subshell. Hence, Calcium has **2 valence electrons**.

The 18 inner-shell (core) electrons, $1s^2 2s^2 2p^6 3s^2 3p^6$, can be replaced by [Ar], see Figure **2.9.3**. The abbreviated notation is: $[Ar]4s^2$

## ✓ Example 2.9.4

Based on their respective locations in the periodic table (use Figure **2.9.3**), determine the number of valence electrons and the valence shell configuration of elements A, B and C.




**Solution**

Element A is located in Period 2, the *5th position* in *2p*-block. Before the electrons are placed in *2p* subshell, the *2s* subshell must be filled first. This means that A has ***two valence electrons*** in 2s ($\mathbf{2s^2}$) and ***five valence electrons*** in 2p ($\mathbf{2p^5}$). Answer: $\mathbf{2s^2 2p^5}$**.** It has ***2 + 5 = 7*** **valence electrons.**

Element B is located in Period 3, the *2nd position* in *3s*-block. This means that B has ***two valence electrons*** in 3s ($\mathbf{3s^2}$). Answer: $\mathbf{3s^2}$**.**

Element C is located in Period 5, the *1st position* in *5s*-block). This means that there is only **one valence electron** in 5s ($\mathbf{5s^1}$). Answer: $\mathbf{5s^1}$.

## 2.9.4Exercise

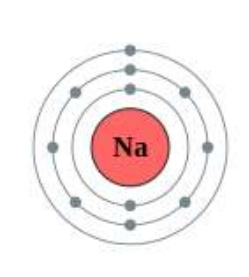
Using the location of Na is the periodic table (Figure **2.9.3**), draw the shell diagram of sodium atom.

**Answer**

Sodium (Na) is the first element in the 3rd row (Period 3) in the periodic table. This means that the first shell and second shells of Na atom are filled to the maximum number of electrons.

The first shell **(1s)** *is filled with* ***2 electrons***. The second shell (2s and 2p) has a **total of *8 electrons***. And, the third (last) shell has ***1 electron***.

The shell diagram of the Na atom is shown below. The shell nearest the nucleus (first shell) has 2 electrons (2 dots), the second shell has 8 electrons and the last (outermost) shell has 1 electron. (**2.8.1**)




## Concept Review Exercises

1. What is the difference between core electrons and valence electrons?

## Answers

1. Electrons are organized into shells and subshells around nuclei.
2. The electron configuration states the arrangement of electrons in shells and subshells.
3. Valence electrons are in the highest-numbered shell; all other electrons are core electrons.

## Key Takeaway

- Electrons are organized into shells and subshells about the nucleus of an atom.
- The valence electrons determine the reactivity of an atom.

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# 2.10: Periodic Trends - Atomic Size and Ionization Energy

**Learning Objectives**

- Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

One of the reasons the periodic table is so useful is because its structure allows us to qualitatively determine how some properties of the elements vary versus their position on the periodic table. The variations of properties versus positions on the periodic table are called **periodic trends**. There is no other tool in science that allows us to judge relative properties of a class of objects like this, which makes the periodic table a very useful tool. Many periodic trends are general. There may be a few points where an opposite trend is seen, but there is an overall trend when considered across a whole row or down a whole column of the periodic table.

## Atomic Radius

The first periodic trend we will consider is atomic radius. The **atomic radius** is an indication of the size of an atom. Although the concept of a definite radius of an atom is a bit fuzzy, atoms behave as if they have a certain radius. Such radii can be estimated from various experimental techniques, such as the x-ray crystallography of crystals.

As you go down a column of the periodic table, the atomic radii increase. This is because the valence electron shell is getting larger and there is a larger principal quantum number, so the valence shell lies physically farther away from the nucleus. This trend can be summarized as follows:

$$as \downarrow PT, atomic\ radius \uparrow$$

where PT stands for periodic table. Going across a row on the periodic table, left to right, the trend is different. Even though the valence shell maintains the same principal quantum number, the number of protons—and hence the nuclear charge—is increasing as you go across the row. The increasing positive charge casts a tighter grip on the valence electrons, so as you go across the periodic table, the atomic radii decrease. Again, we can summarize this trend as follows:

$$as \rightarrow PT, atomic\ radius \downarrow$$

Figure **2.10.1** shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

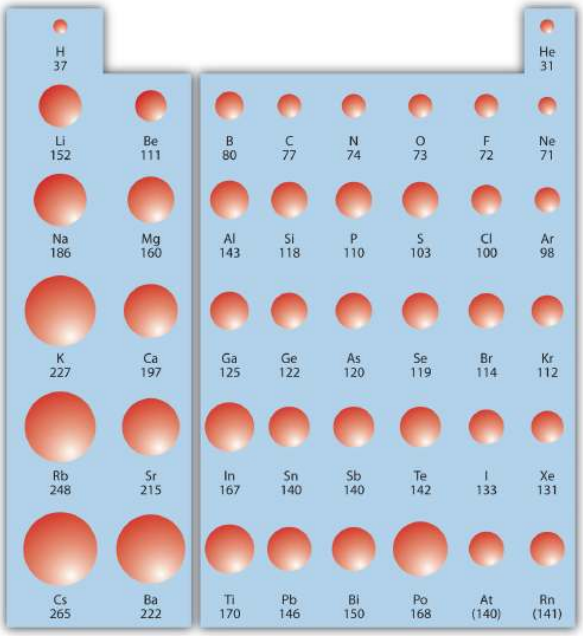



Figure **2.10.1**: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

**Example 2.10.1: Atomic Radii**

Referring only to a periodic table and not to Figure **2.10.1**, which atom is larger in each pair?

a. Si or S
b. S or Te

**Solution**

a. Si is to the left of S on the periodic table; it is larger because as you go across the row, the atoms get smaller.
b. S is above Te on the periodic table; Te is larger because as you go down the column, the atoms get larger.

**Exercise 2.10.1: Atomic Radii**

Referring only to a periodic table and not to Figure **2.10.1**, which atom is smaller, Ca or Br?

**Answer**

Br

## Ionization Energy

**Ionization energy (IE)** is the amount of energy required to remove an electron from an atom in the gas phase:

$$A(g) \rightarrow A^{+}(g) + e^{-} \quad \Delta H \equiv IE$$

IE is usually expressed in kJ/mol of atoms. It is always positive because the removal of an electron always requires that energy be put in (i.e., it is endothermic). IE also shows periodic trends. As you go down the periodic table, it becomes easier to remove an electron from an atom (i.e., IE decreases) because the valence electron is farther away from the nucleus. Thus,

$$as \downarrow PT,\ IE \downarrow$$

However, as you go across the periodic table and the electrons get drawn closer in, it takes more energy to remove an electron; as a result, IE increases:

$$as \rightarrow PT,\ IE \uparrow$$

Figure **2.10.2** shows values of IE versus position on the periodic table. Again, the trend is not absolute, but the general trends going across and down the periodic table should be obvious.

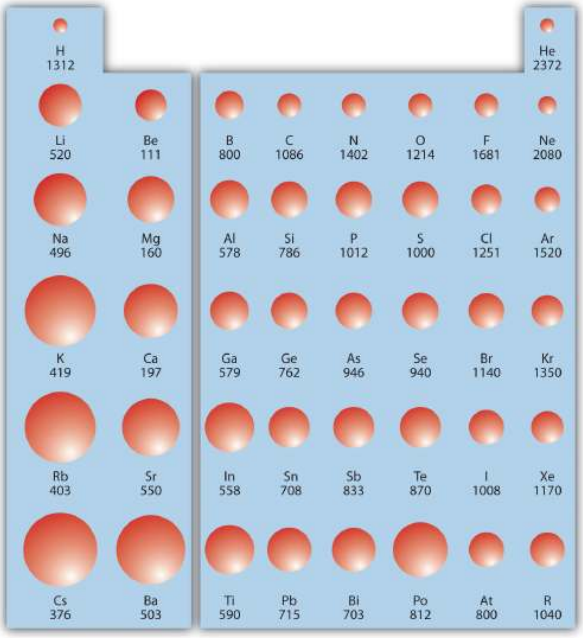



Figure **2.10.2**: Ionization Energy on the Periodic Table. Values are in kJ/mol.

IE also shows an interesting trend within a given atom. This is because more than one IE can be defined by removing successive electrons (if the atom has them to begin with):

- First Ionization Energy ($IE_1$):

$$A(g) \rightarrow A^{+}(g) + e^{-}$$

- Second Ionization Energy ($IE_2$):

$$A^{+}(g) \rightarrow A^{2+}(g) + e^{-}$$

- Third Ionization Energy ($IE_3$):

$$A^{2+}(g) \rightarrow A^{3+}(g) + e^{-}$$

and so forth.

Each successive IE is larger than the previous because an electron is being removed from an atom with a progressively larger positive charge. However, IE takes a large jump when a successive ionization goes down into a new shell. For example, the following are the first three IEs for Mg, whose electron configuration is $1s^2 2s^2 2p^6 3s^2$:

- First Ionization Energy ($IE_1$) = 738 kJ/mol:

$$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$$

- Second Ionization Energy ($IE_2$) = 1,450 kJ/mol:

$$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$$

- Third Ionization Energy ($IE_3$) = 7,734 kJ/mol:

$$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^{-}$$

The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first two electrons are removed from the 3*s* subshell, but the third electron has to be removed from the $n = 2$ shell (specifically, the 2*p* subshell, which is lower in energy than the $n = 3$ shell). Thus, it takes much more energy than just overcoming a larger ionic charge would suggest. It is trends like this that demonstrate that electrons within atoms are organized in groups.

### Example 2.10.2: Ionization Energies

Which atom in each pair has the larger first ionization energy?

a. Ca or Sr
b. K or $K^+$

**Solution**

a. Because Sr is below Ca on the periodic table, it is easier to remove an electron from it; thus, Ca has the higher IE.
b. Because $K^+$ has a positive charge, it will be harder to remove another electron from it, so its IE is larger than that of K. Indeed, it will be significantly larger because the next electron in $K^+$ to be removed comes from another shell.

### Exercise 2.10.2: Ionization Energies

Which atom has the lower ionization energy, C or F?

**Answer**

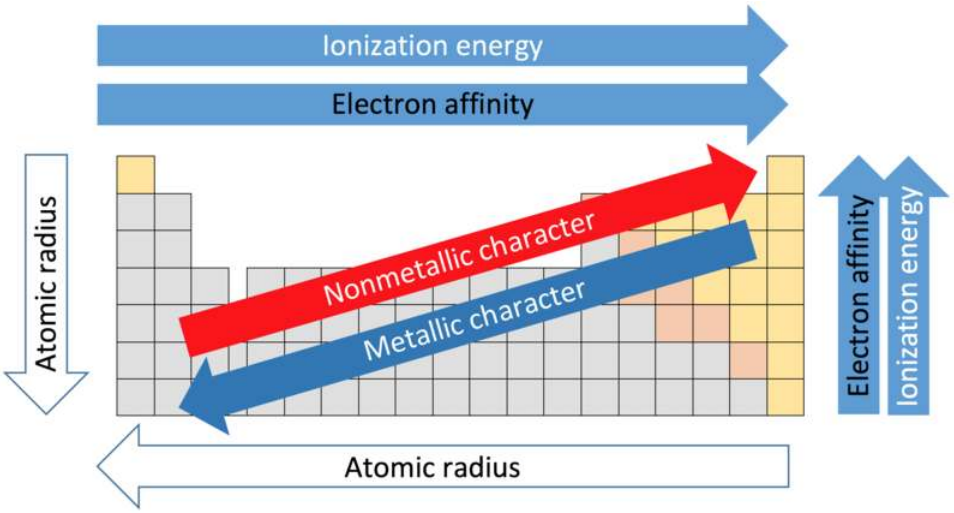
C

### Uses of the Periodic Properties of Elements

1. Predict greater or smaller atomic size and radial distribution in neutral atoms and ions.
2. Measure and compare ionization energies.
3.

## Summary

- Certain properties—notably atomic radius and ionization energies—can be qualitatively understood by the positions of the elements on the periodic table. The major trends are summarized in the figure below.
- There are three factors that help in the prediction of the trends in the Periodic Table: number of protons in the nucleus, number of shells, and shielding effect.




Various periodic trends (CC BY-SA 4.0; Sandbh via Wikipedia)

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# CHAPTER OVERVIEW

## 3: Ionic Compounds


3.1: A Molecular View of Elements and Compounds
3.2: Ionic Bonds
3.3: Ions
3.4: Ions of Some Common Elements
3.5: Polyatomic Ions
3.6: Formulas of Ionic Compounds
3.6.1: Writing Formulas for Ionic Compounds
3.7: Naming Ionic Compounds
3.8: Some Properties of Ionic Compounds


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# 3.1: A Molecular View of Elements and Compounds

**Learning Objectives**

- Classify substances as atomic elements, molecular elements, molecular compounds, or ionic compounds.

## Atomic Elements

Most elements exist with **individual atoms** as their basic unit. It is assumed that there is only one atom in a formula if there is no numerical subscript on the right side of an element's symbol.

## Molecular Elements

There are many substances that exist as two or more atoms connected together so strongly that they behave as a single particle. These multi-atom combinations are called **molecules**. A molecule is the smallest part of a substance that has the physical and chemical properties of that substance. In some respects, a molecule is similar to an atom. A molecule, however, is composed of more than one atom.

Table **3.1.1**: Elements That Exist as Diatomic Molecules

| | | | | | | |
|---|---|---|---|---|---|---|
| Hydrogen, H | Oxygen | Nitrogen | Fluorine | Chlorine | Bromine | Iodine |

Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as diatomic molecules—a molecule with only two atoms (Table **3.1.1**). As with any molecule, these elements are labeled with a **molecular formula**, a formal listing of what and how many atoms are in a molecule. (Sometimes only the word *formula* is used, and its meaning is inferred from the context.) For example, the molecular formula for elemental hydrogen is $H_2$, with H being the symbol for hydrogen and the subscript 2 implying that there are two atoms of this element in the molecule. Other diatomic elements have similar formulas: $O_2$, $N_2$, and so forth. Other elements exist as molecules—for example, sulfur normally exists as an eight-atom molecule, $S_8$, while phosphorus exists as a four-atom molecule, $P_4$ (Figure **3.1.1**).

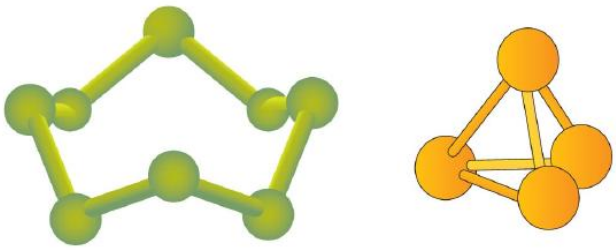


Figure **3.1.1**: Molecular Art of $S_8$ and $P_4$ Molecules. If each green ball represents a sulfur atom, then the diagram on the left represents an $S_8$ molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.

Figure **3.1.1** shows two examples of how molecules will be represented in this text. An atom is represented by a small ball or sphere, which generally indicates where the nucleus is in the molecule. A cylindrical line connecting the balls represents the connection between the atoms that make this collection of atoms a molecule. This connection is called a chemical bond.

## Ionic Compounds

The elements in the periodic table are divided into specific groupings; the metals, the non-metals, the semi-metals, and so on. These groupings are largely based on physical properties and on the tendency of the various elements to bond with other elements by forming either an ionic or a covalent bond. As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). The basic unit of ionic compounds is the **formula unit**.

## Molecular Compounds

Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds. Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals) and silicon dioxide ($SiO_2$) will also be a covalently bound molecule (a semi-metal and a non-metal). The basic unit of molecular compounds is the **molecule**.

### Example 3.1.1

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. Fe
b. $PCl_3$
c. LiBr
d. $P_4$
e. oxygen gas

**Solution**

a. **Fe** (iron) is an element that is represented with no subscript, so it is an **atomic element**.
b. **$PCl_3$** is made up of two nonmetals, so it is a **molecular compound**.
c. **LiBr** is made up of lithium, a metal, and bromine, a nonmetal, so it is an **ionic compound**.
d. **$P_4$** is a substance that is made up of four atoms of the same element, so it is a **molecular element**.
e. The formula for **oxygen gas** is **$O_2$** so it is a molecular element.

### Exercise 3.1.1

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. $I_2$
b. He
c. $H_2O$
d. Al
e. CuCl

**Answer a:**
molecular element

**Answer b:**
atomic element

**Answer c:**
molecular compound

**Answer d:**
atomic element

**Answer e:**
ionic compound

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# 3.2: Ionic Bonds

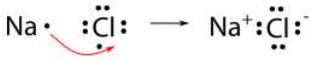
**Learning Objectives**

- Define an ionic bond, ionic compound, and electrostatic force
- Recognize the complexity of three-dimensional ionic bond interactions involved in ionic compounds

## The Ionic Bond

Oppositely charged particles attract each other. This attractive force is often referred to as an **electrostatic force**. An **ionic bond** is the electrostatic electrostatic force that holds ions together in an **ionic compound**. The strength of the ionic bond is directly dependent upon the quantity of the charges and inversely dependent on the distance between the charged particles. A cation with a 2+ charge will make a stronger ionic bond than a cation with a 1+ charge. A larger ion makes a weaker ionic bond because of the greater distance between its electrons and the nucleus of the oppositely charged ion.

We will use sodium chloride as an example to demonstrate the nature of the ionic bond and how it forms. As you know, sodium is a metal and loses its one valence electron to become a cation. Chlorine is a nonmetal and gains one electron in becoming an anion. However, electrons cannot be simply "lost" to nowhere in particular. A more accurate way to describe what is happening is that a single electron is transferred from the sodium atom to the chlorine atom as shown below.



The ionic bond is the attraction of the $Na^+$ ion for the $Cl^-$ ion. It is conventional to show show the cation without dots around the symbol to emphasize that the original energy level that contained the valence electron is now empty. The anion is now shown with a complete octet of electrons.

## Ionic Solids - Lattice Structures

Ionic compounds are held together by attractive electrostatic interactions between cations and anions. In contrast to the simplified electron transfer depicted above for sodium and chlorine, the cations and anions in ionic compounds are arranged in space to form an extended three-dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions (Figure **3.2.1**). In other words, each ion is attracted to many of its neighboring ions forming a sodium chloride crystal or **ionic solid**.

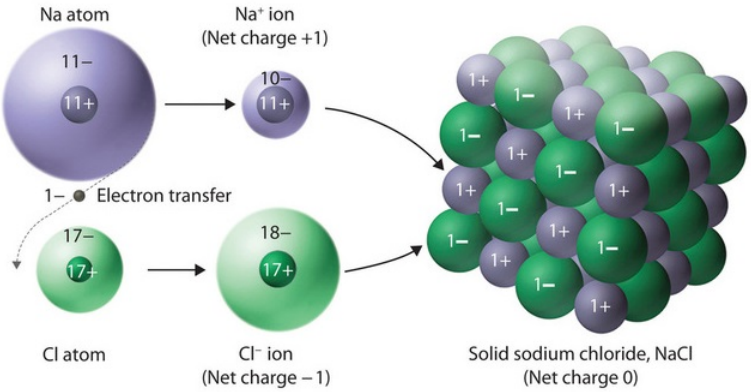



Figure **3.2.1**: Ionic Bonding. The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting $Na^+$ and $Cl^-$ ions form a three-dimensional solid that is held together by attractive electrostatic interactions.

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# 3.3: Ions

**Learning Objectives**

- Distinguish the difference between the two types of ions.
- Describe ion formation using electron configurations.
- Predict ionic charge.

## Ions

As introduced in Chapter 2, atoms contain a nucleus with neutrons and positively charged protons, surrounded by negatively charged electrons. In an atom, the total number of electrons, negative charge, *equals* the total number of protons, positive charge, and therefore, atoms are electrically neutral or uncharged. If an atom loses or gains electrons, it will become a positively or negatively charged particle, called an **ion**. The *loss* of one or more electrons results in more protons than electrons and an overall positively charged ion, called a **cation**. For example, a sodium atom with one less electron is a cation, $Na^+$, with a +1 charge (Figure **3.3.1**).

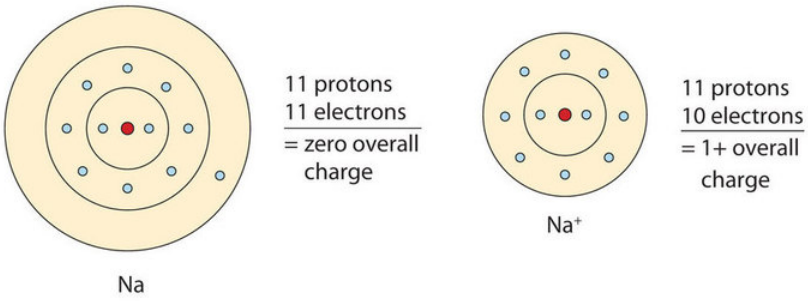



Figure **3.3.1**: On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

When an atom *gains* one or more electrons, it becomes a negatively charged **anion**, because there are more electrons than protons. When chlorine gains one electron it forms a chloride ion, $Cl^-$, with a –1 charge (Figures **3.3.2**)

> The names for positive and negative ions are pronounced CAT-eye-ons (cations) and ANN-eye-ons (anions), respectively.

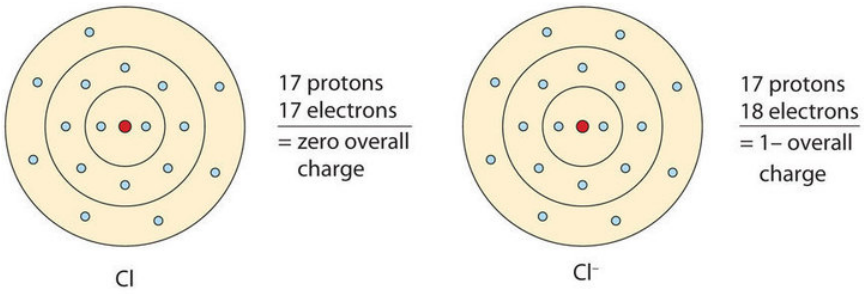



Figure **3.3.2**: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

## Predicting Ionic Charge

Ions are formed when an atom loses or gains electrons. These electrons are usually lost from and gained into the **valence shell**, or outermost energy level. Therefore, it is useful to look at electron configurations to further illustrate ion formation and electron transfer between atoms.

The electron configuration for sodium shows that there are ten core electrons and one valence electron in the third energy level. When sodium loses the single valence electron, forming the cation $Na^+$, the electron configuration is now identical to that of neon, a stable noble gas.

$$\underset{1s^2\,2s^2\,2p^6\,3s^1}{\mathrm{Na}} \rightarrow \underset{1s^2\,2s^2\,2p^6}{\mathrm{Na^+} + \mathrm{e^-}} \tag{3.3.1}$$

Chlorine also has ten core electrons and valence electrons in the third energy level. However, chlorine has seven valence electrons, one less than the noble gas argon, which has eight valence electrons. Thus, chlorine will gain one electron, forming the anion, $Cl^-$, and achieving a stable noble gas configuration.

$$\underset{1s^2\,2s^2\,2p^6\,3s^2\,3p^5}{\mathrm{Cl} + \mathrm{e^-}} \rightarrow \underset{1s^2\,2s^2\,2p^6\,3s^2\,3p^6}{\mathrm{Cl^-}} \tag{3.3.2}$$

> Cations are named using the element name plus "*ion*" to indicate it is charged. Anions are named by changing the element name ending to "*ide*". For example, a magnesium ion is formed when neutral magnesium loses electrons and a fluor*ide* ion is formed when neutral fluorine gains electrons.

When atoms form ions, they tend to reach a full valence shell by gaining enough electrons to have eight electrons in the valence shell or losing the electrons in their original valence shell; the *lower* shell, now the valence shell, has eight electrons in it. For whatever reason, having eight electrons in a valence shell is a particularly energetically stable arrangement of electrons. The trend that atoms like to have eight electrons in their valence shell is called the **octet rule**. When atoms form compounds, the octet rule is not always satisfied for all atoms at all times, but it is a very good rule of thumb for understanding the kinds of bonding arrangements that atoms can make

### 3.3.1 Example

Write the electron configuration of aluminum atom ($Z$ = 13) and underline the valence electrons. How many electrons are gained/lost to form an aluminum ion, $Al^{3+}$? Write the electron configuration for this ion.

**Solution**

The electron configuration of Al atom is $1s^22s^22p^63s^23p^1$. Aluminum has three valence electrons in the third energy level, ($3s^23p^1$). The cation, $Al^{3+}$, is formed when these three valence electrons are **lost**, leaving the configuration for the noble gas neon, $1s^22s^22p^6$.

### 3.3.1 Exercise

Write the electron configuration of oxygen atom ($Z$ = 8) and underline the valence electrons. How many electrons are gained/lost to form an oxide ion, $O^{2-}$? Write the electron configuration for this ion.

**Answer**

The electron configuration of O atom is $1s^22s^22p^4$. Oxygen has six valence electrons in the second energy level, ($2s^22p^4$). The anion $O^{2-}$ is formed when two electrons are gained in the valence shell. The resulting electron configuration, $1s^22s^22p^6$, is also identical to the configuration for the noble gas neon.

## Key Takeaways

- Ions can be positively charged or negatively charged.
- Ionic charge relates to valence electrons and valence shells.

## Contributors

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## Exercises

1. What are the two types of ions?

2. When the following atoms become ions, what charges do they acquire?

a. Li
b. S
c. Ca
d. F

4. Identify each as a cation, an anion, or neither.

a. $H^+$
b. $Cl^-$
c. $O_2$
d. $Ba^{2+}$
e. $CH_4$
f. $CS_2$

5. Identify each as a cation, an anion, or neither.

a. $NH_3$
b. $Br^-$
c. $H^-$
d. $Hg^{2+}$
e. $CCl_4$
f. $SO_3$

6. Write the electron configuration for each ion.

a. $Li^+$
b. $Mg^{2+}$
c. $F^-$
d. $S^{2-}$

7. Write the electron configuration for each ion.

a. $Na^+$
b. $Be^{2+}$
c. $Cl^-$
d. $O^{2-}$

## Answers

1. Cations (positive charged) and anions (negative charged)

2.
   a. 1+
   b. 2−
   c. 2+
   d. 1−

4.
   a. cation

b. anion
c. neither
d. cation
e. neither
f. neither

5.

a. neither
b. anion
c. anion
d. cation
e. neither
f. neither

6.

a. $1s^2$
b. $1s^22s^22p^6$
c. $1s^22s^22p^6$
d. $1s^22s^22p^63s^23p^6$

7.

a. $1s^22s^22p^6$
b. $1s^2$
c. $1s^22s^22p^63s^23p^6$
d. $1s^22s^22p^6$

8.

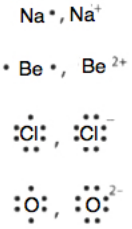
a. $Li\bullet$, $Li^+$

b. $\bullet Mg\bullet$, $Mg^{2+}$

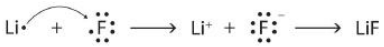
c. 

d. 

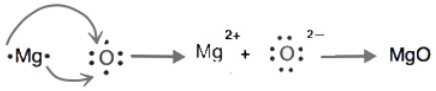
9.



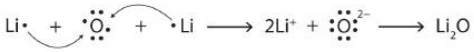
10.



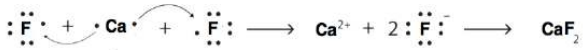
11.



12.



13.



14. 1+

15. 2+

16. 2−

17. 1−

---

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# 3.4: Ions of Some Common Elements

## Learning Objectives

- Become familiar with the charge of some common ions.
- Use the periodic table to predict ion charge.

In many cases, elements that belong to the *same group* (vertical column) on the periodic table form ions with the *same charge* because they have the *same number* of valence electrons. Thus, as introduced previously, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a +1 charge. Ions made from alkaline earth metals, the second group on the periodic table, have a +2 charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a −1 charge. Figure **3.4.1** shows how the charge on many ions can be predicted by the location of an element on the periodic table.

Some elements, especially transition metals, can form ions with variable charges. Figure **3.4.1** shows the characteristic charges for some of these ions. Notice that there is no simple pattern for transition metal ions (or for the larger main group elements) as there is with the main group ions. This is because the transition metals have electrons in *d* subshell and do not follow the octet rule. In order for an element such as iron (Fe) to achieve the same noble gas configuration of argon (Ar), it would need to lose 6 electrons in the *3d* subshell and 2 electrons in the *4s* subshell. An iron ion with a charge of +8 is not very likely, therefore, the octet rule is not applicable to transition elements.

**Note**

For a multiply-charged ion, the correct convention is to write the charge number first followed by the sign. For example, the barium cation is written $Ba^{2+}$, not $Ba^{+2}$.

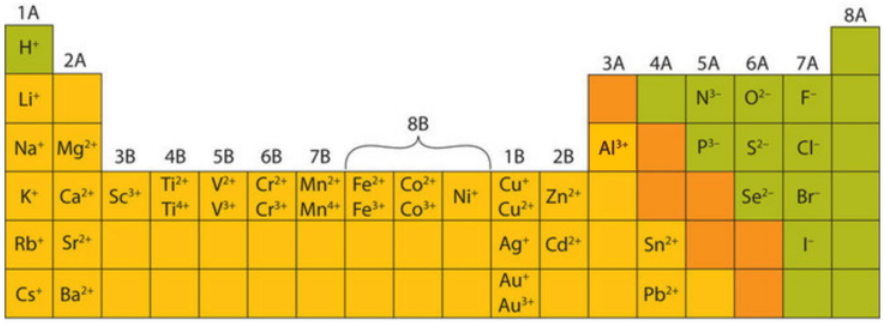



Figure **3.4.1**: Common ions formed by specific elements on the periodic table. The charge that a representative (main group element) acquires when it becomes an ion is related to the location on the periodic table. Note that some metal atoms, specifically the transition elements, commonly form ions with variable charges.

## 3.4.1 Example

Which of these ions is *not likely* to form?

a. $Mg^{+}$
b. $K^{+}$

### Solution

(a) Mg is in Group 2A and has two valence electrons. It achieves octet by losing two electrons to form $Mg^{2+}$ cation. Losing only one electron to form $Mg^{+}$ does not make an octet, hence, $Mg^{+}$ is not likely to form.

## 3.4.2 Exercise

Which of these ions is *not likely* to form?

a. $S^{3-}$

b. $N^{3-}$

**Answer**

(a) S is in Group 6A and has six valence electrons. It achieves octet by gaining two electrons to form $S^{2-}$ anion. Gaining three electrons to form $S^{3-}$does not make it octet, hence, $S^{3-}$ is not likely to form.

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# 3.5: Polyatomic Ions

**Learning Objectives**

- To identify and name polyatomic ions.

Some ions consist of groups of atoms *covalently* bonded together and have an *overall electric charge*. Because these ions contain more than one atom, they are called **polyatomic ions**. The structures, names, and formulas of some polyatomic ions are found in the below figure and table.

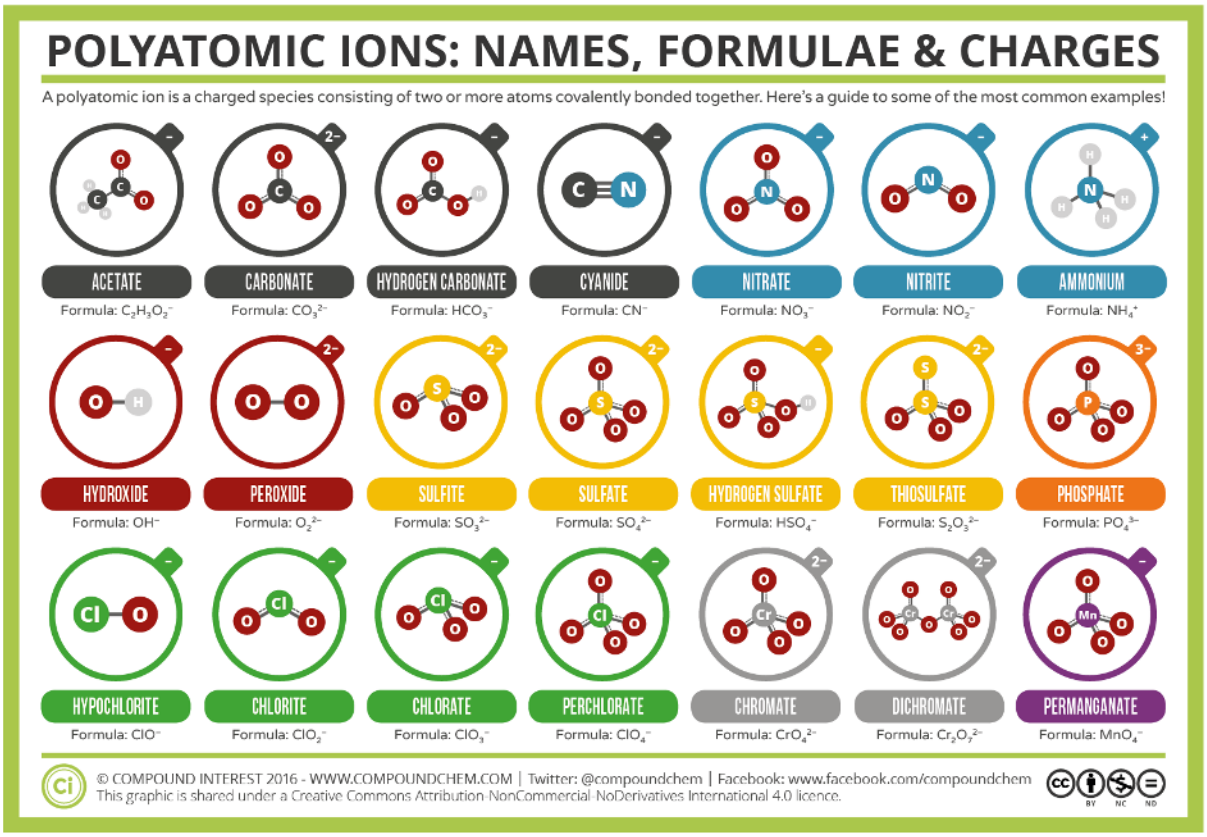



Figure **3.5.1**: Polyatomic Ions Infographic

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table **3.5.1** lists the ion names and ion formulas of the most common polyatomic ions. For example, $\mathbf{NO_3^-}$ is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall −1 charge.

Table **3.5.1**: Common Polyatomic Ion Names and Formulas

| Ion Name | Ion Formula |
|---|---|
| hyddronium ion | $H_3O^+$ |
| ammonium ion | $NH_4^+$ |
| hydroxide ion | $OH^-$ |
| cyanide ion | $CN^-$ |
| carbonate ion | $CO_3^{2-}$ |
| bicarbonate or hydrogen carbonate | $HCO_3^-$ |
| acetate ion | $C_2H_3O_2^-$ **or** $CH_3CO_2^-$ |
| nitr**ate** ion | $NO_3^-$ |
| nitr**ite** ion | $NO_2^-$ |
| sulf**ate** ion | $SO_4^{2-}$ |
| sulf**ite** ion | $SO_3^{2-}$ |
| phosph**ate** ion | $PO_4^{3-}$ |
| phosph**ite** ion | $PO_3^{3-}$ |

Note that only two polyatomic ions in this table are cations, hydronium ion ($H_3O^+$) and ammonium ion ($NH_4^+$), the remaining polyatomic ions are all negatively-charged and, therefore, are classified as anions. However, only two of these, the hydroxide ion and the cyanide ion, are named using the "**-ide**" suffix that is typically indicative of negatively-charged ions. The remaining polyatomic anions, which all contain oxygen, in combination with another non-metal, exist as part of a series in which the number of oxygens within the polyatomic unit can vary. A single suffix, "-ide," is insufficient for distinguishing the names of the anions in a related polyatomic series. Therefore, "**-ate**" and "**-ite**" suffixes are employed, in order to denote that the corresponding polyatomic ions are part of a series. Additionally, these suffixes also indicate the relative number of oxygens that are contained within the polyatomic ions. Note that all of the polyatomic ions whose names end in "-ate" contain one more oxygen than those polyatomic anions whose names end in "-ite." Unfortunately, much like the common system for naming transition metals, these suffixes only indicate the *relative* number of oxygens that are contained within the polyatomic ions. For example, both the nitrate ion, symbolized as $NO_3^-$, and the sulfate ion, symbolized as $SO_4^{2-}$, share an "-ate" suffix, however, the former contains three oxygens, and the latter contains four. Additionally, both the nitrate ion and the sulfite ion contain three oxygens, but these polyatomic ions do not share a common suffix. Unfortunately, the relative nature of these suffixes mandates that the ion formula/ion name combinations of the polyatomic ions must simply be memorized.

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# 3.6: Formulas of Ionic Compounds

**Learning Objectives**

- Write the chemical formula for a simple ionic compound.
- Recognize polyatomic ions in chemical formulas.

We have already encountered some chemical formulas for simple ionic compounds. A chemical formula is a concise list of the elements in a compound and the ratios of these elements. To better understand what a chemical formula means, we must consider how an ionic compound is constructed from its ions.

## Formula Unit

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 3.6.1). As you can see, there are no individual NaCl "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use NaCl (one Na symbol and one Cl symbol) to represent the compound. Thus, NaCl is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that NaCl crystals are composed of individual NaCl units, Figure 3.6.1 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

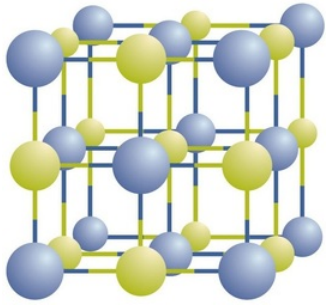


Figure 3.6.1: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

## Ionic Compound Formula

The formula for an ionic compound follows several conventions. First, the **cation** is written **before** the **anion**. Because most metals form cations and most nonmetals form anions, formulas typically list the metal first and then the nonmetal. Second, **charges** are **not written** in a formula. Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. Finally, the proper formula for an ionic compound always has ***a net zero charge,*** meaning the total positive charge must equal the total negative charge. To determine the proper formula of any combination of ions, determine how many of each ion is needed to balance the total positive and negative charges in the compound.

> *This rule is ultimately based on the fact that matter is, overall, electrically neutral.*

By convention, assume that there is only one atom if a subscript is not present. We do not use 1 as a subscript.

If we look at the ionic compound consisting of lithium ions and bromide ions, we see that the lithium ion has a 1+ charge and the bromide ion has a 1− charge. Only one ion of each is needed to balance these charges. The formula for lithium bromide is LiBr.

When an ionic compound is formed from magnesium and oxygen, the magnesium ion has a 2+ charge, and the oxygen atom has a 2− charge. Although both of these ions have higher charges than the ions in lithium bromide, they still balance each other in a one-

to-one ratio. Therefore, the proper formula for this ionic compound is **MgO**.

Now consider the ionic compound formed by magnesium and chlorine. A magnesium ion has a 2+ charge, while a chlorine ion has a 1− charge:

$$\mathbf{Mg^{2+}Cl^{-}} \tag{3.6.1}$$

Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:

$$\mathbf{Mg^{2+}\ Cl^{-}\ Cl^{-}} \tag{3.6.2}$$

Now the positive and negative charges are balanced. We could write the chemical formula for this ionic compound as **MgClCl**, but the convention is to use a numerical subscript when there is more than one ion of a given type—$\mathbf{MgCl_2}$. This chemical formula says that there are one magnesium ion and *two* chloride ions in this formula. (Do not read the "$Cl_2$" part of the formula as a molecule of the diatomic elemental chlorine. Chlorine does not exist as a diatomic element in this compound. Rather, it exists as two individual chloride ions.) By convention, the **lowest whole number ratio** is used in the formulas of ionic compounds. The formula $\mathbf{Mg_2Cl_4}$ has balanced charges with the ions in a 1:2 ratio, but it is not the lowest whole number ratio.

> By convention, the lowest whole-number ratio of the ions is used in ionic formulas. There are exceptions for certain ions, such as $\mathbf{Hg_2^{2+}}$.

For compounds in which the ratio of ions is not as obvious, the subscripts in the formula can be obtained by **crossing charges**: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically in Figure 3.3.2.

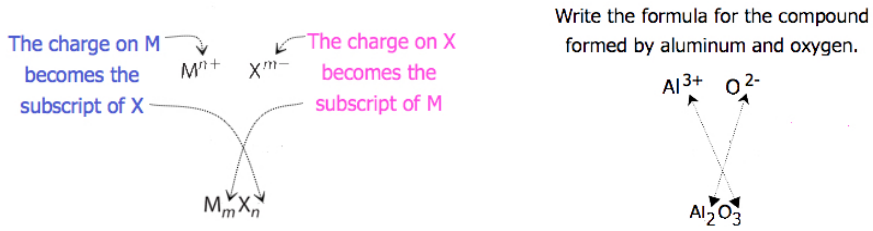



Figure **3.6.2**: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

When crossing charges, it is sometimes necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by $Pb^{4+}$ and $O^{2-}$. Using the absolute values of the charges on the ions as subscripts gives the formula $Pb_2O_4$. This simplifies to its correct empirical formula $\mathbf{PbO_2}$. The empirical formula has one $Pb^{4+}$ ion and two $O^{2-}$ ions.

## 3.6.1 Example

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the sodium ion and the sulfur ion
b. the aluminum ion and the fluoride ion
c. the 3+ iron ion and the oxygen ion

### Solution

a. To obtain a valence shell octet, sodium forms an ion with a 1+ charge, while the sulfur ion has a 2− charge. Two sodium 1+ ions are needed to balance the 2− charge on the sulfur ion. Rather than writing the formula as **NaNaS**, we shorten it by convention to $\mathbf{Na_2S}$.
b. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1− charge. Three fluorine 1− ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as $\mathbf{AlF_3}$.

c. Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxygen atom has a 2− charge as an ion. To balance the positive and negative charges, we look to the least common multiple—6: two iron 3+ ions will give 6+, while three 2− oxygen ions will give 6−, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is $\mathbf{Fe_2O_3}$. Alternatively, use the crossing charges method shown in Figure 3.3.2.

### 3.6.1 Exercise

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the calcium ion and the oxygen ion
b. the 2+ copper ion and the sulfur ion
c. the 1+ copper ion and the sulfur ion

**Answer a:**

CaO

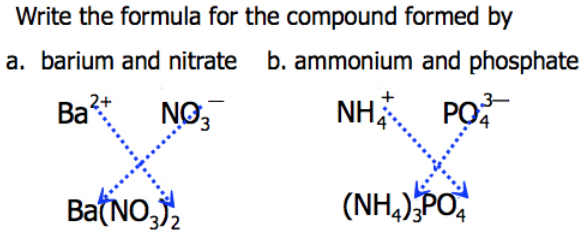
**Answer b:**

CuS

**Answer c:**

$Cu_2S$

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. Two examples are shown below:




### 3.6.2 Example

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the potassium ion and the sulfate ion
b. the calcium ion and the nitrate ion

**Solution**

a. Potassium ions have a charge of 1+, while sulfate ions have a charge of 2−. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is $\mathbf{K_2SO_4}$.
b. Calcium ions have a charge of 2+, while nitrate ions have a charge of 1−. We will need two nitrate ions to balance the charge on each calcium ion. The formula for nitrate must be enclosed in parentheses. Thus, we write $\mathbf{Ca(NO_3)_2}$ as the formula for this ionic compound.

### 3.6.2 Exercise

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the magnesium ion and the carbonate ion
b. the aluminum ion and the acetate ion

**Answer a:**

$Mg^{2+}$ and $CO_3^{2-} = MgCO_3$

**Answer b:**

$Al^{3+}$ and $C_2H_3O_2^- = Al(C_2H_3O_2)_3$

## Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between **metal and nonmetal** elements are usually **ionic**. For example, $CaBr_2$ contains a metallic element (calcium, a group 2A metal) and a nonmetallic element (bromine, a group 7A nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound $NO_2$ contains two elements that are both nonmetals (nitrogen, from group 5A, and oxygen, from group 6A). It is not an ionic compound; it belongs to the category of covalent compounds discuss elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Second, if you recognize the formula of a **polyatomic ion** in a compound, the compound is **ionic**. For example, if you see the formula $Ba(NO_3)_2$, you may recognize the "$NO_3$" part as the nitrate ion, $NO_3^-$. (Remember that the convention for writing formulas for ionic compounds is not to include the ionic charge.) This is a clue that the other part of the formula, Ba, is actually the $Ba^{2+}$ ion, with the 2+ charge balancing the overall 2− charge from the two nitrate ions. Thus, this compound is also ionic.

### 3.6.3 Example

Identify each compound as ionic or not ionic.

a. $Na_2O$
b. $PCl_3$
c. $NH_4Cl$
d. $OF_2$

**Solution**

a. Sodium is a metal, and oxygen is a nonmetal; therefore, $Na_2O$ is expected to be ionic.
b. Both phosphorus and chlorine are nonmetals. Therefore, $PCl_3$ is not ionic.
c. The $NH_4$ in the formula represents the ammonium ion, $NH_4^+$, which indicates that this compound is ionic.
d. Both oxygen and fluorine are nonmetals. Therefore, $OF_2$ is not ionic.

### 3.6.3 Exercise

Identify each compound as ionic or not ionic.

a. $N_2O$
b. $FeCl_3$
c. $(NH_4)_3PO_4$
d. $SOCl_2$

**Answer a:**

not ionic

**Answer b:**

ionic

**Answer c:**

ionic

**Answer d:**

not ionic

### Looking Closer: Blood and Seawater

Science has long recognized that blood and seawater have similar compositions. After all, both liquids have ionic compounds dissolved in them. The similarity may be more than mere coincidence; many scientists think that the first forms of life on Earth arose in the oceans. A closer look, however, shows that blood and seawater are quite different. A 0.9% solution of sodium chloride approximates the salt concentration found in blood. In contrast, seawater is principally a 3% sodium chloride solution, over three times the concentration in blood. Here is a comparison of the amounts of ions in blood and seawater:

| Ion | Percent in Seawater | Percent in Blood |
|---|---|---|
| $Na^+$ | 2.36 | 0.322 |
| $Cl^-$ | 1.94 | 0.366 |
| $Mg^{2+}$ | 0.13 | 0.002 |
| $SO_4^{2-}$ | 0.09 | — |
| $K^+$ | 0.04 | 0.016 |
| $Ca^{2+}$ | 0.04 | 0.0096 |
| $HCO_3^-$ | 0.002 | 0.165 |
| $HPO_4^{2-}$, $H_2PO_4^-$ | — | 0.01 |

Most ions are more abundant in seawater than they are in blood, with some important exceptions. There are far more hydrogen carbonate ions ($\mathbf{HCO_3^-}$) in blood than in seawater. This difference is significant because the hydrogen carbonate ion and some related ions have a crucial role in controlling the acid-base properties of blood. The amount of hydrogen phosphate ions—$\mathbf{HPO_4^{2-}}$ and $\mathbf{H_2PO_4^-}$—in seawater is very low, but they are present in higher amounts in blood, where they also affect acid-base properties. Another notable difference is that blood does not have significant amounts of the sulfate ion ($\mathbf{SO_4^{2-}}$), but this ion is present in seawater.

## Key Takeaways

- Proper chemical formulas for ionic compounds balance the total positive charge with the total negative charge.
- Groups of atoms with an overall charge, called polyatomic ions, also exist.

## EXERCISES

1. What information is contained in the formula of an ionic compound?
2. Why do the chemical formulas for some ionic compounds contain subscripts, while others do not?
3. Write the chemical formula for the ionic compound formed by each pair of ions.
   a. $Mg^{2+}$ and $I^-$
   b. $Na^+$ and $O^{2-}$
4. Write the chemical formula for the ionic compound formed by each pair of ions.
   a. $Na^+$ and $Br^-$
   b. $Mg^{2+}$ and $Br^-$
   c. $Mg^{2+}$ and $S^{2-}$
5. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $K^+$ and $Cl^-$
b. $Mg^{2+}$ and $Cl^-$
c. $Mg^{2+}$ and $Se^{2-}$

6. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $Na^+$ and $N^{3-}$
b. $Mg^{2+}$ and $N^{3-}$
c. $Al^{3+}$ and $S^{2-}$

7. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $Li^+$ and $N^{3-}$
b. $Mg^{2+}$ and $P^{3-}$
c. $Li^+$ and $P^{3-}$

8. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $Fe^{3+}$ and $Br^-$
b. $Fe^{2+}$ and $Br^-$
c. $Au^{3+}$ and $S^{2-}$
d. $Au^+$ and $S^{2-}$

9. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $Cr^{3+}$ and $O^{2-}$
b. $Cr^{2+}$ and $O^{2-}$
c. $Pb^{2+}$ and $Cl^-$
d. $Pb^{4+}$ and $Cl^-$

10. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $Cr^{3+}$ and $NO_3^-$
b. $Fe^{2+}$ and $PO_4^{3-}$
c. $Ca^{2+}$ and $CrO_4^{2-}$
d. $Al^{3+}$ and $OH^-$

11. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $NH_4^+$ and $NO_3^-$
b. $H^+$ and $Cr_2O_7^{2-}$
c. $Cu^+$ and $CO_3^{2-}$
d. $Na^+$ and $HCO_3^-$

12. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

a. Ba and S
b. Cs and I

13. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

a. K and S
b. Sc and Br

14. Which compounds would you predict to be ionic?

a. $Li_2O$
b. $(NH_4)_2O$
c. $CO_2$

d. $FeSO_3$
e. $C_6H_6$
f. $C_2H_6O$

15. Which compounds would you predict to be ionic?

a. $Ba(OH)_2$
b. $CH_2O$
c. $NH_2CONH_2$
d. $(NH_4)_2CrO_4$
e. $C_8H_{18}$
f. $NH_3$

## Answers

1. the ratio of each kind of ion in the compound

2. Sometimes more than one ion is needed to balance the charge on the other ion in an ionic compound.

3.

a. $MgI_2$
b. $Na_2O$

4.

a. NaBr
b. $MgBr_2$
c. MgS

5.

a. KCl
b. $MgCl_2$
c. MgSe

6.

a. $Na_3N$
b. $Mg_3N_2$
c. $Al_2S_3$

7.

a. $Li_3N$
b. $Mg_3P_2$
c. $Li_3P$

8.

a. $FeBr_3$
b. $FeBr_2$
c. $Au_2S_3$
d. $Au_2S$

9.

a. $Cr_2O_3$
b. $CrO$
c. $PbCl_2$
d. $PbCl_4$

10.

a. $Cr(NO_3)_3$
b. $Fe_3(PO_4)_2$
c. $CaCrO_4$
d. $Al(OH)_3$

11.

a. $NH_4NO_3$
b. $H_2Cr_2O_7$
c. $Cu_2CO_3$
d. $NaHCO_3$

12.

a. $Ba^{2+}$, $S^{2-}$, $BaS$
b. $Cs^{+}$, $I^{-}$, $CsI$

13.

a. $K^{+}$, $S^{2-}$, $K_2S$
b. $Sc^{3+}$, $Br^{-}$, $ScBr_3$

14.

a. ionic
b. ionic
c. not ionic
d. ionic
e. not ionic
f. not ionic

15.

a. ionic
b. not ionic
c. not ionic
d. ionic
e. not ionic
f. not ionic

---

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# 3.6.1: Writing Formulas for Ionic Compounds

**Learning Objectives**

- Write the correct formula for an ionic compound.
- Recognize polyatomic ions in chemical formulas.

Ionic compounds do not exist as molecules. In the solid state, ionic compounds are in crystal lattice containing many ions each of the cation and anion. An ionic formula, like $NaCl$, is an empirical formula. This formula merely indicates that sodium chloride is made of an equal number of sodium and chloride ions. Sodium sulfide, another ionic compound, has the formula $Na_2S$. This formula indicates that this compound is made up of twice as many sodium ions as sulfide ions. This section will teach you how to find the correct ratio of ions, so that you can write a correct formula.

## Writing Formulas for Ionic Compounds with Monatomic Ions

If you know the name of a binary ionic compound, you can write its **chemical formula**. Start by writing the metal ion with its charge, followed by the nonmetal ion with its charge. Because the overall compound must be electrically neutral, decide how many of each ion is needed in order for the positive and negative charges to cancel each other out.

**Example 3.6.1.1: Aluminum Nitride and Lithium Oxide**

Write the formulas for aluminum nitride and lithium oxide.

**Solution**

Solution to Example 5.5.1

| | Write the formula for aluminum nitride | Write the formula for lithium oxide |
|---|---|---|
| 1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second. | $Al^{3+}$ $N^{3-}$ | $Li^{+}$ $O^{2-}$ |
| 2. Use a multiplier to make the total charge of the cations and anions equal to each other. | total charge of cations = total charge of anions<br>1(3+) = 1(3-)<br>+3 = -3 | total charge of cations = total charge of anions<br>2(1+) = 1(2-)<br>+2 = -2 |
| 3. Use the multipliers as subscript for each ion. | $Al_1N_1$ | $Li_2O_1$ |
| 4. Write the final formula. Leave out all charges and all subscripts that are 1. | $AlN$ | $Li_2O$ |

An alternative way to writing a correct formula for an ionic compound is to use the **crisscross method**. In this method, the numerical value of each of the ion charges is crossed over to become the subscript of the other ion. Signs of the charges are dropped.

**Example 3.6.1.2: The Crisscross Method for Lead (IV) Oxide**

Write the formula for lead (IV) oxide.

**Solution**

Solution to Example 5.5.2

| Crisscross Method | Write the formula for lead (IV) oxide |
|---|---|
| 1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second. | $Pb^{4+}$ $O^{2-}$ |
| 2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation. |   |
| 3. Reduce to the lowest ratio. | $Pb_2O_4$ |
| 4. Write the final formula. Leave out all subscripts that are 1. | $PbO_2$ |

**? Exercise 3.6.1.2**

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the calcium ion and the oxygen ion
b. the 2+ copper ion and the sulfur ion
c. the 1+ copper ion and the sulfur ion

**Answer a:**

CaO

**Answer b:**

CuS

**Answer c:**

$Cu_2S$

> *Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions.*

**✓ Example 3.6.1.3: Sulfur Compound**

Write the formula for sodium combined with sulfur.

**Solution**

Solution to Example 5.5.3

| Crisscross Method | Write the formula for sodium combined with sulfur |
|---|---|
| 1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second. | $Na^{+}$ $S^{2-}$ |
| 2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation. |   |
| 3. Reduce to the lowest ratio. | This step is not necessary. |
| 4. Write the final formula. Leave out all subscripts that are 1. | $Na_2S$ |

**? Exercise 3.6.1.3**

Write the formula for each ionic compound.

a. sodium bromide

b. lithium chloride
c. magnesium oxide

**Answer a:**
NaBr
**Answer b:**
LiCl
**Answer c:**
MgO

## Polyatomic Ions

Some ions consist of groups of atoms bonded together and have an overall electric charge. Because these ions contain more than one atom, they are called polyatomic ions. Polyatomic ions have characteristic formulas, names, and charges that should be memorized. For example, $NO_3^-$ is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Table **3.6.1.1** lists the most common polyatomic ions.

Table **3.6.1.1**: Some Polyatomic Ions

| Name | Formula |
|---|---|
| ammonium ion | $NH_4^+$ |
| acetate ion | $C_2H_3O_2^-$ (also written $CH_3CO_2^-$) |
| carbonate ion | $CO_3^{2-}$ |
| chromate ion | $CrO_4^{2-}$ |
| dichromate ion | $Cr_2O_7^{2-}$ |
| hydrogen carbonate ion (bicarbonate ion) | $HCO_3^-$ |
| cyanide ion | $CN^-$ |
| hydroxide ion | $OH^-$ |
| nitrate ion | $NO_3^-$ |
| nitrite ion | $NO_2^-$ |
| permanganate ion | $MnO_4^-$ |
| phosphate ion | $PO_4^{3-}$ |
| hydrogen phosphate ion | $HPO_4^{2-}$ |
| dihydrogen phosphate ion | $H_2PO_4^-$ |
| sulfate ion | $SO_4^{2-}$ |
| hydrogen sulfate ion (bisulfate ion) | $HSO_4^-$ |
| sulfite ion | $SO_3^{2-}$ |

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. An example is $Ba(NO_3)_2$.

## Writing Formulas for Ionic Compounds Containing Polyatomic Ions

Writing a formula for ionic compounds containing polyatomic ions also involves the same steps as for a binary ionic compound. Write the symbol and charge of the cation followed by the symbol and charge of the anion.

### Example 3.6.1.4: Calcium Nitrate

Write the formula for calcium nitrate.

**Solution**

Solution to Example 5.5.4

| Crisscross Method | Write the formula for calcium nitrate |
|---|---|
| 1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second. | $Ca^{2+}$ $NO_3^-$ |
| 2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation. |   The 2+ charge on Ca becomes the subscript of NO3 and the 1- charge on NO3 becomes the subscript of Ca. |
| 3. Reduce to the lowest ratio. | $Ca_1(NO_3)_2$ |
| 4. Write the final formula. Leave out all subscripts that are 1. If there is only 1 of the polyatomic ion, leave off parentheses. | $Ca(NO_3)_2$ |

### Example 3.6.1.5

Write the chemical formula for an ionic compound composed of the potassium ion and the sulfate ion.

**Solution**

Solution to Example 5.5.5

| Explanation | Answer |
|---|---|
| Potassium ions have a charge of 1+, while sulfate ions have a charge of 2−. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is $K_2SO_4$. | $K_2SO_4$ |

### Exercise 3.6.1.5

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the magnesium ion and the carbonate ion
b. the aluminum ion and the acetate ion

**Answer a:**

$MgCO_3$

**Answer b:**

$Al(CH_3COO)_3$

## Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between metal and nonmetal elements are usually ionic. For example, $CaBr_2$ contains a metallic element (calcium, a group 2 [or 2A] metal) and a nonmetallic element (bromine, a group 17 [or

7A] nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound $NO_2$ contains two elements that are both nonmetals (nitrogen, from group 15 [or 5A], and oxygen, from group 16 [or 6A]. It is not an ionic compound; it belongs to the category of covalent compounds discussed elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Second, if you recognize the formula of a polyatomic ion in a compound, the compound is ionic. For example, if you see the formula $Ba(NO_3)_2$, you may recognize the "$NO_3$" part as the nitrate ion, $NO_3^-$. (Remember that the convention for writing formulas for ionic compounds is not to include the ionic charge.) This is a clue that the other part of the formula, Ba, is actually the $Ba^{2+}$ ion, with the 2+ charge balancing the overall 2− charge from the two nitrate ions. Thus, this compound is also ionic.

### Example 3.6.1.6

Identify each compound as ionic or not ionic.

a. $Na_2O$
b. $PCl_3$
c. $NH_4Cl$
d. $OF_2$

**Solution**

Solution to Example 5.5.6

| Explanation | Answer |
|---|---|
| a. Sodium is a metal, and oxygen is a nonmetal. Therefore, $Na_2O$ is expected to be ionic. | $Na_2O$, ionic |
| b. Both phosphorus and chlorine are nonmetals. Therefore, $PCl_3$ is not ionic. | $PCl_3$, not ionic |
| c. The $NH_4$ in the formula represents the ammonium ion, $NH_4^+$, which indicates that this compound is ionic. | $NH_4Cl$, ionic |
| d. Both oxygen and fluorine are nonmetals. Therefore, $OF_2$ is not ionic. | $OF_2$, ionic |

### Exercise 3.6.1.6

Identify each compound as ionic or not ionic.

a. $N_2O$
b. $FeCl_3$
c. $(NH_4)_3PO_4$
d. $SOCl_2$

**Answer a:**

not ionic

**Answer b:**

ionic

**Answer c:**

ionic

**Answer d:**

not ionic

## Summary

Formulas for ionic compounds contain the symbols and number of each atom present in a compound in the lowest whole number ratio.

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# 3.7: Naming Ionic Compounds

**Learning Objectives**

- To use the rules for naming ionic compounds.

After learning a few more details about the names of individual ions, you will be one step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

## Naming Ions

The name of a monatomic cation is simply the name of the element followed by the word *ion*. Thus, $Na^+$ is the sodium ion, $Al^{3+}$ is the aluminum ion, $Ca^{2+}$ is the calcium ion, and so forth.

We have seen that some elements lose different numbers of electrons, producing ions of different charges (Figure 3.3). Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish $Fe^{2+}$ from $Fe^{3+}$. The same issue arises for other ions with more than one possible charge.

There are two ways to make this distinction. In the simpler, more modern approach, called the **Stock system**, an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word *ion*. Thus, $Fe^{2+}$ is called the iron(II) ion, while $Fe^{3+}$ is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the $Na^+$ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

Table **3.7.1**: The Modern and Common System of Cation Names

| Element | Stem | Charge | Modern Name | Common Name |
|---|---|---|---|---|
| iron | ferr- | 2+ | iron(II) ion | ferrous ion |
| | | 3+ | iron(III) ion | ferric ion |
| copper | cupr- | 1+ | copper(I) ion | cuprous ion |
| | | 2+ | copper(II) ion | cupric ion |
| tin | stann- | 2+ | tin(II) ion | stannous ion |
| | | 4+ | tin(IV) ion | stannic ion |
| lead | plumb- | 2+ | lead(II) ion | plumbous ion |
| | | 4+ | lead(IV) ion | plumbic ion |
| chromium | chrom- | 2+ | chromium(II) ion | chromous ion |
| | | 3+ | chromium(III) ion | chromic ion |
| gold | aur- | 1+ | gold(I) ion | aurous ion |
| | | 3+ | gold(III) ion | auric ion |

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table **3.7.1** lists the elements that use the common system, along with their respective cation names.

Table **3.7.2**: Some Monatomic Anions

| Ion | Name |
|---|---|
| $F^-$ | fluoride ion |
| $Cl^-$ | chloride ion |
| $Br^-$ | bromide ion |
| $I^-$ | iodide ion |
| $O^{2-}$ | oxide ion |
| $S^{2-}$ | sulfide ion |
| $P^{3-}$ | phosphide ion |
| $N^{3-}$ | nitride ion |

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, $Cl^-$ is "chlor-" + "-ide ion," or the chloride ion. Similarly, $O^{2-}$ is the oxide ion, $Se^{2-}$ is the selenide ion, and so forth. Table **3.7.2** lists the names of some common monatomic ions. The polyatomic ions have their own characteristic names, as discussed earlier.

### ✔ Example 3.7.1

Name each ion.

a. $Ca^{2+}$
b. $S^{2-}$
c. $SO_3^{2-}$
d. $NH_4^+$
e. $Cu^+$

**Solution**

a. the calcium ion
b. the sulfide ion
c. the sulfite ion
d. the ammonium ion
e. the copper(I) ion or the cuprous ion

### ? Exercise 3.7.1

Name each ion.

a. $Fe^{2+}$
b. $Fe^{3+}$
c. $SO_4^{2-}$
d. $Ba^{2+}$
e. $HCO_3^-$

**Answer a:**

iron(II) ion

**Answer b:**

iron(III) ion

**Answer c:**

sulfate ion

**Answer d:**

barium ion

**Answer e:**

hydrogen carbonate ion or bicarbonate ion

**Example 3.7.2**

Write the formula for each ion.

a. the bromide ion
b. the phosphate ion
c. the cupric ion
d. the magnesium ion

**Solution**

a. $Br^-$
b. $PO_4^{3-}$
c. $Cu^{2+}$
d. $Mg^{2+}$

**Exercise 3.7.2**

Write the formula for each ion.

a. the fluoride ion
b. the carbonate ion
c. the stannous ion
d. the potassium ion

**Answer a:**

$F^-$

**Answer b:**

$CO_3^{2-}$

**Answer c:**

$Sn^{2+}$

**Answer d:**

$K^+$

## Naming Binary Ionic Compounds with a Metal that Forms Only One Type of Cation

A **binary** ionic compound is a compound composed of a **monatomic** metal **cation** and a monatomic nonmetal **anion**. The metal cation is named first, followed by the nonmetal anion as illustrated in Figure **3.7.1** for the compound $BaCl_2$. The word *ion* is dropped from both parts.

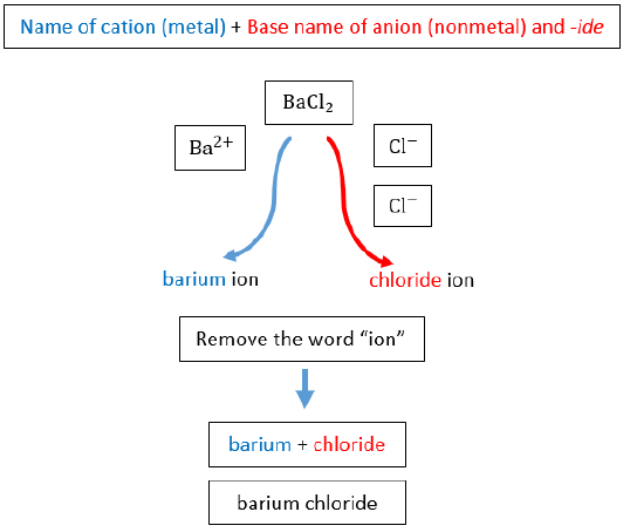



Figure **3.7.1**: Naming $BaCl_2$
Naming formula: Name of metal cation + base
name of nonmetal anion + suffix -ide. BaCl2 is named as barium chloride.

Subscripts in the formula do not affect the name.

### ✔ Example 3.7.3: Naming Ionic Compounds

Name each ionic compound.

a. $CaCl_2$
b. $AlF_3$
c. KCl

**Solution**

a. Using the names of the ions, this ionic compound is named calcium chloride.
b. The name of this ionic compound is aluminum fluoride.
c. The name of this ionic compound is potassium chloride

### ? Exercise 3.7.3

Name each ionic compound.

a. AgI
b. MgO
c. $Ca_3P_2$

**Answer a:**
silver iodide

**Answer b:**
magnesium oxide

**Answer c:**
calcium phosphide

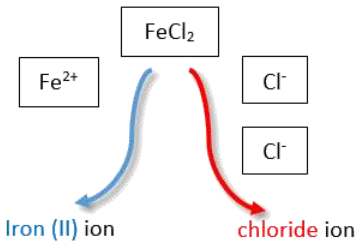
## Naming Binary Ionic Compounds with a Metal That Forms More Than One Type of Cation

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $FeCl_2$ and $FeCl_3$. In the first compound, the iron

ion has a 2+ charge because there are two $Cl^-$ ions in the formula (1− charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three $Cl^-$ ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride (Figure **3.7.2**).

Table **3.7.3**: Naming the $FeCl_2$ and $FeCl_3$ Compounds in the Modern/Stock System.

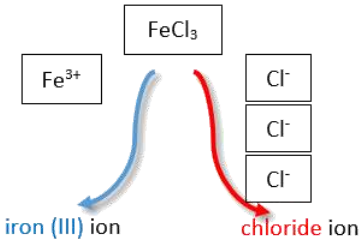
**Name of cation (metal) + (Roman Numeral in parenthesis) + Base name of anion (nonmetal) and *-ide***




Remove the word "ion"

iron (II) + chloride

iron (II) chloride




Remove the word "ion"

iron (III) + chloride

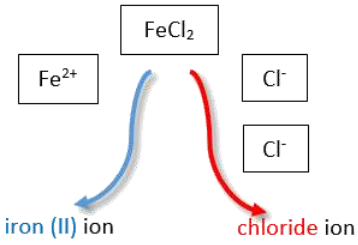
iron (III) chloride

If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively (Figure **3.7.3**) .

Table **3.7.4**: Naming the $FeCl_2$ and $FeCl_3$ Compounds in the Old/Common System.

**"Old" base name of cation (metal) and *-ic or -ous* + Base name of anion (nonmetal) and *-ide***

-ous (for ions with lower charge)

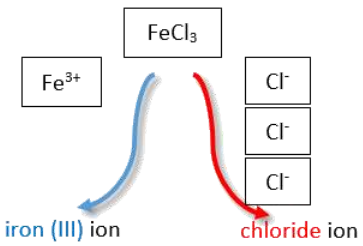



Remove the word "ion"

ferrous + chloride

ferrous chloride

-ic (for ions with higher charge)




Remove the word "ion"

ferric + chloride

ferric chloride

**Example 3.7.4:**

Name each ionic compound.

a. $Co_2O_3$
b. FeCl2

**Solution**

Solutions to Example 5.7.4

| | Explanation | Answer |
|---|---|---|
| **a** | We know that cobalt can have more than one possible charge; we just need to determine what it is.<br>• Oxide always has a 2− charge, so with three oxide ions, we have a total negative charge of 6−.<br>• This means that the two cobalt ions have to contribute 6+, which for two cobalt ions means that each one is 3+.<br>• Therefore, the proper name for this ionic compound is cobalt(III) oxide. | cobalt(III) oxide |
| **b** | Iron can also have more than one possible charge.<br>• Chloride always has a 1− charge, so with two chloride ions, we have a total negative charge of 2−.<br>• This means that the one iron ion must have a 2+ charge.<br>• Therefore, the proper name for this ionic compound is iron(II) chloride. | iron(II) chloride |

**Exercise 3.7.4**

Name each ionic compound.

a. $AuCl_3$
b. $PbO_2$
c. CuO

**Answer a:**

gold(III) chloride

**Answer b:**

lead(IV) oxide

**Answer c:**

copper(II) oxide

## Naming Ionic Compounds with Polyatomic Ions

The process of naming ionic compounds with polyatomic ions is the same as naming binary ionic compounds. The cation is named first, followed by the anion. One example is the ammonium sulfate compound in Figure **3.7.6**.

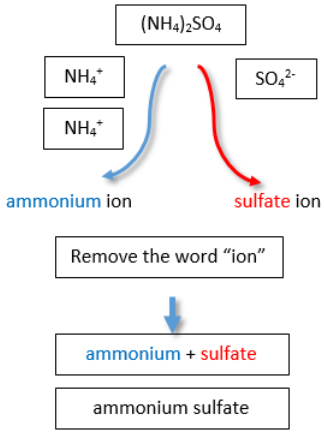



Figure **3.7.2**: Naming Ionic Compounds with Polyatomic Ions

## Example 3.7.5: Naming Ionic Compounds

Write the proper name for each ionic compound.

a. $(NH_4)_2S$
b. $AlPO_4$,
c. $Fe_3(PO_4)_2$

### Solution

Solutions to Example 5.7.5

| Explanation | Answer |
|---|---|
| a. The ammonium ion has a 1+ charge and the sulfide ion has a 2− charge.<br>Two ammonium ions need to balance the charge on a single sulfide ion.<br>The compound's name is ammonium sulfide. | ammonium sulfide |
| b. The ions have the same magnitude of charge, one of each (ion) is needed to balance the charges.<br>The name of the compound is aluminum phosphate. | aluminum phosphate |
| c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6.<br>To get 6+, three iron(II) ions are needed, and to get 6−, two phosphate ions are needed .<br>The compound's name is iron(II) phosphate. | iron(II) phosphate |

## Exercise 3.7.5A

Write the proper name for each ionic compound.

a. $(NH_4)_3PO_4$
b. $Co(NO_2)_3$

**Answer a:**

ammonium phosphate

**Answer b:**

cobalt(III) nitrite

Figure **3.7.1** is a synopsis of how to name simple ionic compounds.

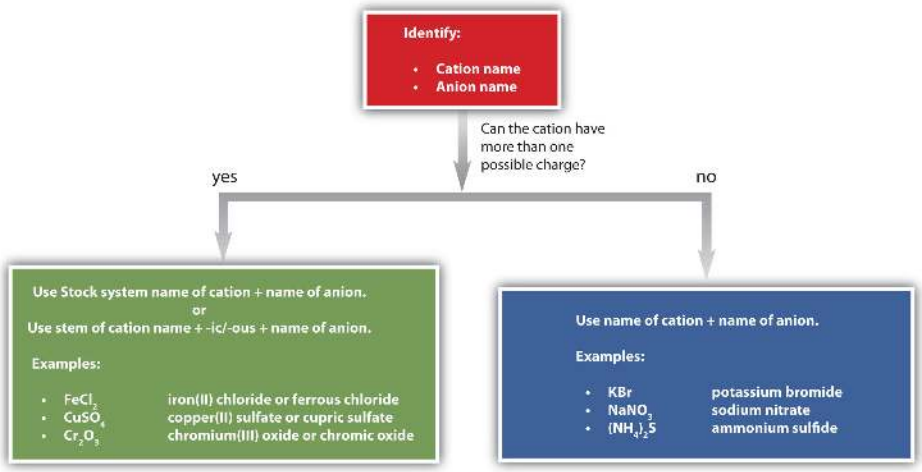



Figure **3.7.3**: A Guide to Naming Simple Ionic Compounds.

## ? Exercise 3.7.5*B*

Name each ionic compound.

a. $ZnBr_2$
b. $Al_2O_3$
c. $(NH_4)_3PO_4$
d. $AuF_3$
e. AgF

**Answer a:**

zinc bromide

**Answer b:**

aluminum oxide

**Answer c:**

ammonium phosphate

**Answer d:**

gold(III) fluoride or auric fluoride

**Answer e:**

silver fluoride

## Summary

- Ionic compounds are named by stating the cation first, followed by the anion.
- Positive and negative charges must balance.
- Some anions have multiple forms and are named accordingly with the use of roman numerals in parentheses.
- Ternary compounds are composed of three or more elements.

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# 3.8: Some Properties of Ionic Compounds

**Learning Objectives**

- Describe the basic physical properties of ionic compounds.

The figure below shows just a few examples of the color and brilliance of naturally occurring ionic crystals. The regular and orderly arrangement of ions in the crystal lattice is responsible for the various shapes of these crystals, while transition metal ions give rise to the colors.

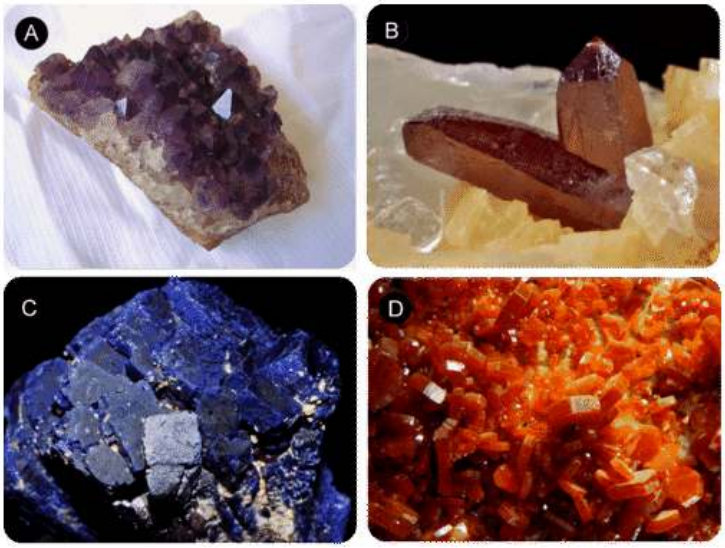



Figure **3.8.1**: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz, $SiO_2$, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral, $Cu_3(CO_3)_2(OH)_2$. (D) Vanadinite - the primary ore of vanadium, $Pb_3(VO_4)_3Cl$.*

## Melting Points

Because of the many simultaneous attractions between cations and anions that occur, ionic crystal lattices are very strong. The process of melting an ionic compound requires the addition of large amounts of energy in order to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about 800 $^oC$. As a comparison, the molecular compound water melts at 0 °C.

## Shattering

Ionic compounds are generally hard, but **brittle.** Why? It takes a large amount of mechanical force, such as striking a crystal with a hammer, to force one layer of ions to shift relative to its neighbor. However, when that happens, it brings ions of the same charge next to each other (see below). The repulsive forces between like-charged ions cause the crystal to shatter. When an ionic crystal breaks, it tends to do so along smooth planes because of the regular arrangement of the ions.

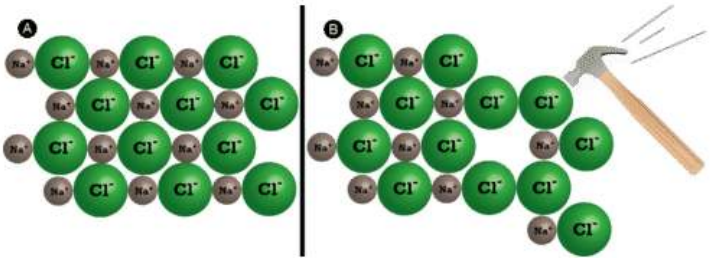



Figure **3.8.2**: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

## Conductivity

Another characteristic property of ionic compounds is their **electrical conductivity**. The figure below shows three experiments in which two electrodes that are connected to a light bulb are placed in beakers containing three different substances.

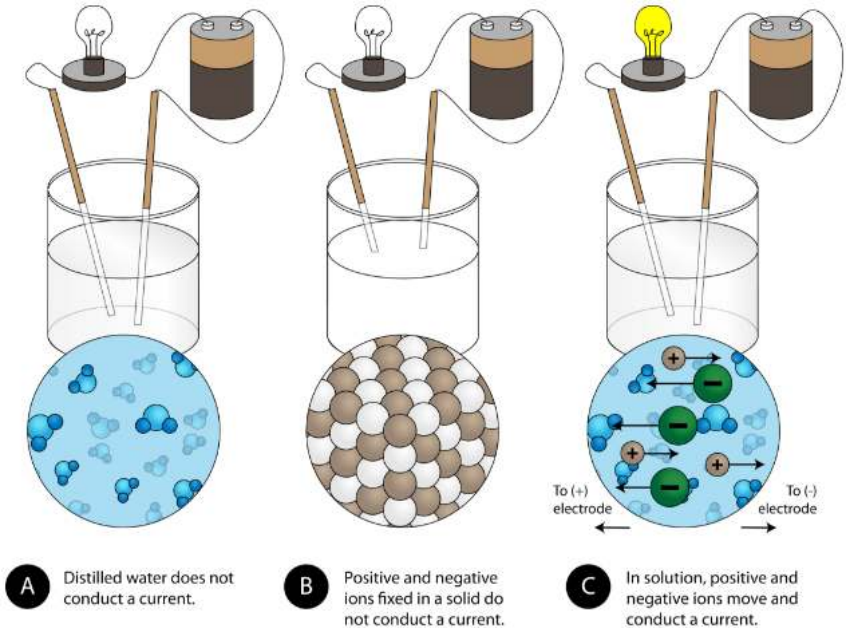



Figure **3.8.3**: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

In the first beaker, distilled water does not conduct a current because water is a molecular compound. In the second beaker, solid sodium chloride also does not conduct a current. Despite being ionic and thus composed of charged particles, the solid crystal lattice does not allow the ions to move between the electrodes. Mobile charged particles are required for the circuit to be complete and the light bulb to light up. In the third beaker, the NaCl has been dissolved into the distilled water. Now the crystal lattice has been broken apart and the individual positive and negative ions can move.

### ✔ Example 3.8.1

Write the dissociation equation of solid NaCl in water.

**Solution**

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

### ? Exercise 3.8.1

Write the dissociation equation of solid $NH_4NO_3$ in water.

**Answer**

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

## Key Takeaways

- Ionic compounds have high melting points.
- Ionic compounds are hard and brittle.
- Ionic compounds dissociate into ions when dissolved in water.
- Solutions of ionic compounds and melted ionic compounds conduct electricity, but solid materials do not.
- An ionic compound can be identified by its chemical formula: metal + nonmetal or polyatomic ions.

## Contributors and Attributions

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# CHAPTER OVERVIEW

## 4: Covalent Compounds


4.1: Covalent Bonds
4.2: Naming Molecular Compounds
4.3: Representing Valence Electrons with Dots
4.4: Covalent Lewis Structures- Electrons Shared
4.5: Writing Lewis Structures for Covalent Compounds
4.6: Resonance - Equivalent Lewis Structures for the Same Molecule
4.7: Predicting the Shapes of Molecules
4.8: Electronegativity and Polarity - Why Oil and Water Do not Mix


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# 4.1: Covalent Bonds

**Learning Objectives**

- Describe how covalent bonds form using the octet rule.

## Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an $H_2$ molecule; each hydrogen atom in the $H_2$ molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about $7.4 \times 10^{-11}$ m, or 74 picometers (pm; 1 pm = $1 \times 10^{-12}$ m). This particular bond length represents the lowest potential energy state of two hydrogen atoms and is a balance between several forces: the ***attractions*** between oppositely charged electrons and nuclei, the ***repulsion*** between two negatively charged electrons, and the ***repulsion*** between two positively charged nuclei.

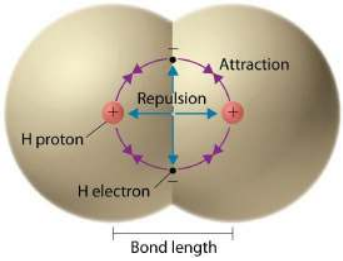



Figure **4.1.1**: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure **4.1.2**) shows that energy decreases as two hydrogen atoms move toward each other. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases.

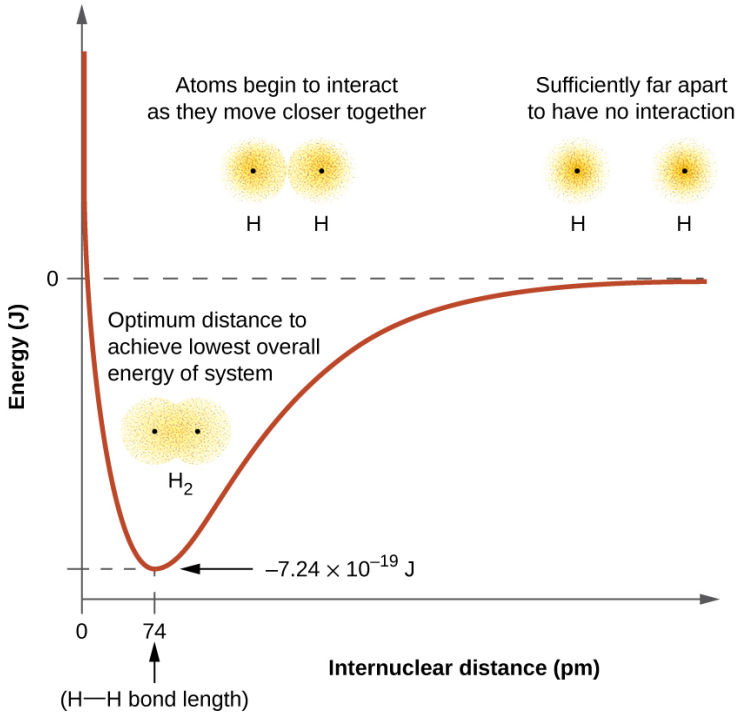



Figure **4.1.2**: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the $H_2$ molecule.

## Lewis Structures

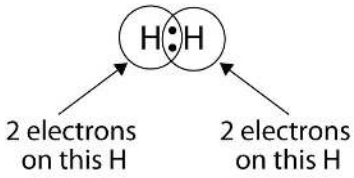
Chemists frequently use Lewis structures to represent covalent bonding in molecular substances. For example, the Lewis symbols of two separate hydrogen atoms are as follows:

$$H\bullet \qquad\qquad \bullet H$$

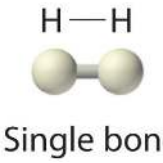
The Lewis structures of two hydrogen atoms sharing electrons looks like this:

$$H{:}H$$

We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:




Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. For simplicity's sake, it is common to represent the covalent bond with a dash, instead of with two dots:




Single bond

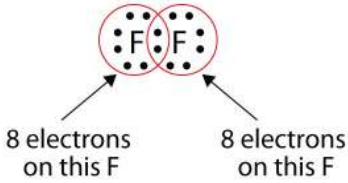
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



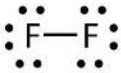

These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.




Note that each F atom has a *complete octet* around it now:




We can also write this using a dash to represent the shared electron pair:




You will notice that there are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three lone pairs of electrons.

## Diatomic Molecules

Hydrogen ($\mathbf{H_2}$) and fluorine ($\mathbf{F_2}$) are both described as *diatomic molecules*. These elements and others (see Table **4.1.1**) exist naturally as molecules rather than as individual atoms. It is important to note that the names of these elements represent molecules and not individual atoms. When describing a single atom rather than a molecule, the word atom is used.

Table **4.1.1**: Elements That Exist as Diatomic Molecules

| | | | |
|---|---|---|---|
| Hydrogen ($\mathbf{H_2}$) | Oxygen ($\mathbf{O_2}$) | Nitrogen ($\mathbf{N_2}$) | Fluorine ($\mathbf{F_2}$) |
| Chlorine ($\mathbf{Cl_2}$) | Bromine ($\mathbf{Br_2}$) | Iodine ($\mathbf{I_2}$) | |

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# 4.2: Naming Molecular Compounds

**Learning Objectives**

- Determine the name of a simple molecular compound from its chemical formula.

## Molecular Compounds

Molecular compounds are inorganic compounds that take the form of discrete **molecules**. Examples include such familiar substances as water ($H_2O$) and carbon dioxide ($CO_2$). These compounds are very different from ionic compounds like sodium chloride ($NaCl$). Ionic compounds are formed when metal atoms lose one or more of their electrons to nonmetal atoms. The resulting cations and anions are electrostatically attracted to each other.

So what holds the atoms of a molecule together? Rather than forming ions, the atoms of a molecule share their **electrons** in such a way that a **bond** forms between a pair of atoms. In a carbon dioxide molecule, there are two of these bonds, each occurring between the carbon atom and one of the two oxygen atoms.

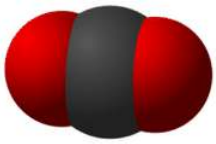


Figure **4.2.1**: Carbon dioxide molecules consist of a central carbon atom bonded to 2 oxygen atoms.

Larger molecules can have many, many bonds that serve to keep the molecule together. In a large sample of a given molecular compound, all of the individual molecules are identical.

## Naming Binary Molecular Compounds

Recall that a molecular formula shows the number of atoms of each element that a molecule contains. A molecule of water contains two hydrogen atoms and one oxygen atom, so its formula is $H_2O$. A molecule of octane, which is a component of gasoline, contains 8 atoms of carbon and 18 atoms of hydrogen. The molecular formula of octane is $C_8H_{18}$.



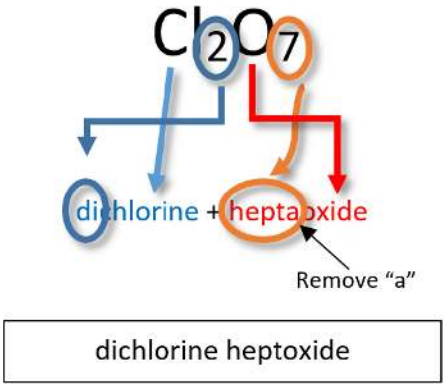
Figure **4.2.2**: Nitrogen dioxide ($NO_2$) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines.

Naming *binary* (two-element) molecular compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table **4.2.1** lists these numerical prefixes.

Table **4.2.1**: Numerical Prefixes for Naming Binary Covalent Compounds

| Number of Atoms in Compound | Prefix on the Name of the Element |
|---|---|
| 1 | mono-* |
| 2 | di- |
| 3 | tri- |
| 4 | tetra- |
| 5 | penta- |
| 6 | hexa- |
| 7 | hepta- |
| 8 | octa- |
| 9 | nona- |
| 10 | deca- |

*This prefix is not used for the first element's name.




**Note**

- Generally, the less electronegative element is written first in the formula, though there are a few exceptions. Carbon is always first in a formula and hydrogen is after nitrogen in a formula such as $NH_3$. The order of common nonmetals in binary compound formulas is C, P, N, H, S, I, Br, Cl, O, F.
- The *a* or *o* at the end of a prefix is usually dropped from the name when the name of the element begins with a vowel. As an example, four oxygen atoms, is tetr**o**xide instead of tetr**ao**xide.
- The prefix is "mono" is not added to the first element's name if there is only one atom of the first element in a molecule.

Some examples of molecular compounds are listed in Table 4.2.2.

Table 4.2.2

| Formula | Name |
|---|---|
| NO | nitrogen monoxide |
| $N_2O$ | dinitrogen monoxide |
| $S_2Cl_2$ | disulfur dichloride |
| $Cl_2O_7$ | dichlorine heptoxide |

Notice that the *mono-* prefix is not used with the nitrogen in the first compound, but is used with the oxygen in both of the first two examples. The $S_2Cl_2$ emphasizes that the formulas for molecular compounds are not reduced to their lowest ratios. The *o* of the *mono-* and the *a* of *hepta-* are dropped from the name when paired with oxide.

**? Exercise 4.2.1**

Write the name for each compound.

a. $CF_4$
b. $SeCl_2$
c. $SO_3$

**Answer a:**

carbon tetrafluoride

**Answer b:**

selenium dichloride

**Answer c:**

sulfur trioxide

## Simple molecular compounds with common names

For some simple covalent compounds, we use common names rather than systematic names. We have already encountered these compounds, but we list them here explicitly:

- $H_2O$: water
- $NH_3$: ammonia
- $CH_4$: methane
- $H_2O_2$: hydrogen peroxide

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system.

## Some Compounds Have Both Covalent and Ionic Bonds

If you recall the introduction of polyatomic ions, you will remember that the bonds that hold the polyatomic ions together are covalent bonds. Once the polyatomic ion is constructed with covalent bonds, it reacts with other substances as an ion. The bond between a polyatomic ion and another ion will be ionic. An example of this type of situation is in the compound sodium nitrate. Sodium nitrate is composed of a sodium ion and a nitrate ion. The nitrate ion is held together by covalent bonds and the nitrate ion is attached to the sodium ion by an ionic bond.

## Summary

- A molecular compound is usually composed of two or more nonmetal elements.
- Molecular compounds are named with the first element first and then the second element by using the stem of the element name plus the suffix -ide. Numerical prefixes are used to specify the number of atoms in a molecule.

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# 4.3: REPRESENTING VALENCE ELECTRONS WITH DOTS

**LEARNING OBJECTIVE**

- Draw a Lewis electron dot diagram for an atom or a monatomic ion.

In almost all cases, chemical bonds are formed by interactions of valence electrons in atoms. To facilitate our understanding of how valence electrons interact, a simple way of representing those valence electrons would be useful.

## LEWIS DOT DIAGRAMS

A **Lewis electron dot diagram** (or electron dot diagram, or a Lewis diagram, or a Lewis structure) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (The order in which the positions are used does not matter.) For example, the Lewis electron dot diagram for hydrogen is simply

$$\mathbf{H}\cdot$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\mathbf{H}} \quad \textit{or} \quad \cdot\mathbf{H} \quad \textit{or} \quad \underset{\cdot}{\mathbf{H}}$$

The electron dot diagram for helium, with two valence electrons, is as follows:

$$\mathbf{He:}$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the 1*s* subshell; this is the common convention we will adopt, although there will be exceptions later. The next atom, lithium, has an electron configuration of $1s^2 2s^1$, so it has only one electron in its valence shell. Its electron dot diagram resembles that of hydrogen, except the symbol for lithium is used:

$$\mathbf{Li}\cdot$$

Beryllium has two valence electrons in its 2*s* shell, so its electron dot diagram is like that of helium:

$$\mathbf{Be:}$$

The next atom is boron. Its valence electron shell is $2s^2 2p^1$, so it has three valence electrons. The third electron will go on another side of the symbol:

$$\dot{\mathbf{B}}\mathbf{:}$$

Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are four valence electrons, two in the 2*s* subshell and two in the 2*p* subshell. As usual, we will draw two dots together on one side, to represent the 2*s* electrons. However, conventionally, we draw the dots for the two *p* electrons on different sides. As such, the electron dot diagram for carbon is as follows:

$$\cdot\dot{\mathbf{C}}\mathbf{:}$$

With N, which has three *p* electrons, we put a single dot on each of the three remaining sides:

$$\cdot\dot{\underset{\cdot}{\mathbf{N}}}\mathbf{:}$$

For oxygen, which has four *p* electrons, we now have to start doubling up on the dots on one other side of the symbol. When doubling up electrons, make sure that each side has no more than two electrons.

$$\cdot\ddot{\underset{\cdot}{\mathbf{O}}}\mathbf{:}$$

Fluorine and neon have seven and eight dots, respectively:

$$\mathbf{:}\ddot{\underset{\cdot}{\mathbf{F}}}\mathbf{:}$$

$$\mathbf{:}\ddot{\underset{\cdot\,\cdot}{\mathbf{Ne}}}\mathbf{:}$$

With the next element, sodium, the process starts over with a single electron because sodium has a single electron in its highest-numbered shell, the $n = 3$ shell. By going through the periodic table, we see that the Lewis electron dot diagrams of atoms will never have more than eight dots around the atomic symbol.

## EXAMPLE 4.3.1: LEWIS DOT DIAGRAMS

What is the Lewis electron dot diagram for each element?

a. aluminum
b. selenium

### Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 3*s* electrons:



2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the $n = 4$ shell, there are six electrons. Its electron dot diagram is as follows:



## EXERCISE 4.3.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

**Answer a**



**Answer b**



## SUMMARY

- Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.
- Lewis electron dot diagrams for ions have less (for cations) or more (for anions) dots than the corresponding atom.

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# 4.4: Covalent Lewis Structures- Electrons Shared

**Learning Objectives**

- Define *covalent bond*.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons and another atom to gain one or more electrons. However, some atoms won't give up or gain electrons easily. Yet they still participate in compound formation. How? There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they make a bond called a **covalent bond**.

## Lewis Dot Diagrams and Covalent Bonding

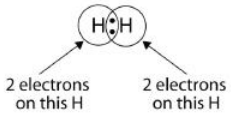
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H}\cdot \quad \cdot\mathbf{H}$$

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

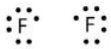
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:




Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

H–H

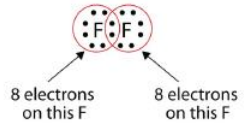
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:




These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.




Note that each F atom has a complete octet around it now:

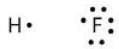



We can also write this using a dash to represent the shared electron pair:

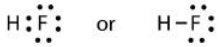


There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:



The two atoms can share their unpaired electrons to make a covalent bond:




We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

**Example 4.4.1:**

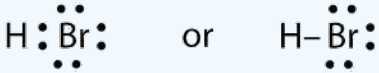
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

**Solution**

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:



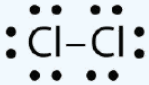
The two atoms can share their unpaired electron:




**Exercise 4.4.1**

Use Lewis electron dot diagrams to illustrate the covalent bond formation in $Cl_2$.

**Answer**



When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far, and there are still some electrons that remain unattached. You can't just leave them there. So where do you put them?

## Multiple Covalent Bonds

Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of $\mathbf{C_2H_4}$. The carbon atoms are bonded together, with each carbon also bonded to two hydrogen atoms.

two **C** atoms $= 2 \times 4 = 8$ valence electrons

four **H** atoms $= 4 \times 1 = 4$ valence electrons

total of 12 valence electrons in the molecule

If the Lewis electron dot structure was drawn with a single bond between the carbon atoms and with the octet rule followed, it would look like this:

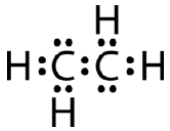


Figure **4.4.1**: Incorrect dot structure of ethene. (CK12 License)

This Lewis structure is incorrect because it contains a total of 14 electrons. However, the Lewis structure can be changed by eliminating the lone pairs on the carbon atoms and having to share two pairs instead of only one pair.

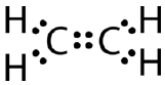


Figure **4.4.2**: Correct dot structure for ethene. (CK12 License)

A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethane can also be represented by a structural formula and with a molecular model as shown in the figure below.

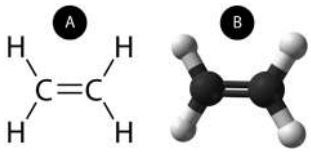



Figure **4.4.3**: (A) The structural model for $C_2H_4$ consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of $C_2H_4$.

A **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. The element nitrogen is a gas that composes the majority of Earth's atmosphere. A nitrogen atom has five valence electrons, which can be shown as one pair and three single electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.

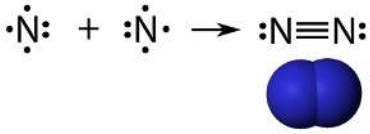


Figure **4.4.4**: Triple bond in $N_2$.

Each nitrogen atom follows the octet rule with one lone pair of electrons, and six electrons that are shared between the atoms.

## Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

## Contributions & Attributions

- 
- Anonymous by request

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# 4.5: Writing Lewis Structures for Covalent Compounds

**Learning Objectives**

- Draw Lewis structures for covalent compounds.

## Writing Lewis Structures

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions.

**How-to: Constructing Lewis electron structures**

**1. 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.

**2. 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.

**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.

**7. Final check**

- Always make sure all valence electrons are accounted for and that each atom has an octet of electrons, except for hydrogen (with two electrons).
- The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

**Example 4.5.1: Water**

Write the Lewis Structure for $H_2O$.

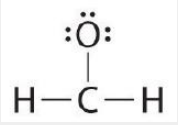
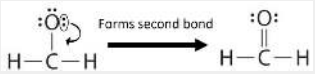
**Solution**

| Steps for Writing Lewis Structures | Example **4.5.1** |
|---|---|
| 1. Determine the total number of valence electrons in the molecule or ion. | 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. |
| 2. Arrange the atoms to show specific connections. | H O H<br>Because H atoms are almost always terminal, the arrangement within the molecule must be HOH. |
| 3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.<br>4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen). | Placing one bonding pair of electrons between the O atom and each H atom gives<br>H -O- H<br>with 4 electrons left over.<br>Each H atom has a full valence shell of 2 electrons. |
| 5. If any electrons are left over, place them on the central atom. | Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:<br>  |
| 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. | Not necessary. |
| 7. Final check. | The Lewis structure gives oxygen an octet and each hydrogen 2 electrons. |

**Example 4.5.2**

Write the Lewis structure for the $CH_2O$ molecule

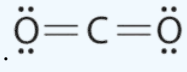
**Solution**

| Steps for Writing Lewis Structures | Example 4.5.2 |
|---|---|
| 1. Determine the total number of valence electrons in the molecule or ion. | Each hydrogen atom (group 1) has 1 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. |
| 2. Arrange the atoms to show specific connections. |  Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. |
| 3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. | Placing a bonding pair of electrons between each pair of bonded atoms gives the following:  6 electrons are used, and 6 are left over. |
| 4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen). | 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. If any electrons are left over, place them on the central atom. | Not necessary. There are no electrons left to place on the central atom. |
| 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. | 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:   |
| 7. Final check | 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. |

**? Exercise 4.5.1**

Write Lewis electron structures for $CO_2$ and $SCl_2$, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

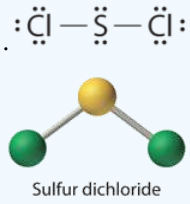
**Answer $CO_2$**





Carbon dioxide

**Answer $SCl_2$**




The United States Supreme Court has the unenviable task of deciding what the law is. This responsibility can be a major challenge when there is no clear principle involved or where there is a new situation not encountered before. Chemistry faces the same challenge in extending basic concepts to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

## Writing Lewis Structures for Polyatomic Ions (CK-12)

Recall that a polyatomic ion is a group of atoms that are covalently bonded together and which carry an overall electrical charge. The ammonium ion, $NH_4^+$, is formed when a hydrogen ion ($H^+$) attaches to the lone pair of an ammonia ($NH_3$) molecule in a coordinate covalent bond.

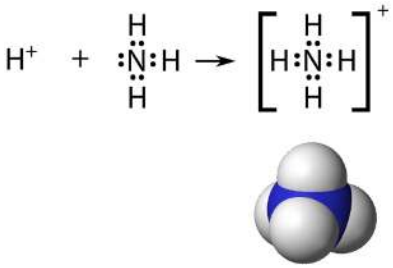


Figure **4.5.3**: The ammonium ion. (CK12 License)

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$1\ \text{N atom} = 5 \text{ valence electrons}$$

$$4\ \text{H atoms} = 4 \times 1 = 4 \text{ valence electrons}$$

subtract 1 electron for the $1+$ charge of the ion

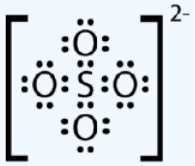
total of 8 valence electrons in the ion

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside of the brackets.

**Exercise 4.5.2**

Draw the Lewis electron dot structure for the sulfate ion.

**Answer (CK12 License)**



## Exceptions to the Octet Rule (BC Campus)

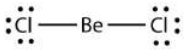
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

There are three violations to the octet rule. Odd-electron molecules represent the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are NO, $NO_2$, and $ClO_2$. The Lewis electron dot diagram for NO is as follows:

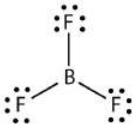


Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

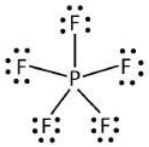
Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:




Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is $BF_3$:




The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called expanded valence shell molecules. Such compounds are formed only by central atoms in the third row of the periodic table or beyond that have empty *d* orbitals in their valence shells that can participate in covalent bonding. One such compound is $PF_5$. The only reasonable Lewis electron dot diagram for this compound has the P atom making five covalent bonds:




Formally, the P atom has 10 electrons in its valence shell.

### Example 4.5.3: Octet Violations

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

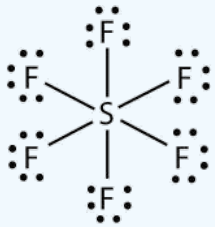
a. ClO
b. $SF_6$

**Solution**

a. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:



b. In $SF_6$, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:




**? Exercise 4.5.3: Xenon Difluoride**

Identify the violation to the octet rule in $XeF_2$ by drawing a Lewis electron dot diagram.

**Answer**




The Xe atom has an expanded valence shell with more than eight electrons around it.

## Summary

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. Lewis structures for polyatomic ions follow the same rules as those for other covalent compounds. There are three violations to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules.

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# 4.6: Resonance - Equivalent Lewis Structures for the Same Molecule

**Learning Objectives**

- Explain the concept of resonance and how it works with within molecules.

## Resonance

There are some cases in which more than one viable Lewis structure can be drawn for a molecule. An example is the ozone ($O_3$) molecule in Figure **4.6.1**. There are a total of 18 electrons in the structure and so the following two structures are possible.

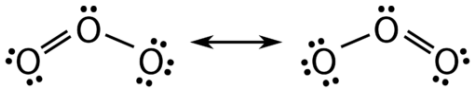


Figure **4.6.1**: Resonance forms of ozone. Note the use of the double-headed arrow.

The structure on the left (**4.6.1**) can be converted to the structure on the right by a shifting of electrons without altering the positions of the atoms.

It was once thought that the structure of a molecule such as $O_3$ consisted of one single bond and one double bond which then shifted back and forth as shown above. However, further studies showed that the two bonds are identical. Any double covalent bond between two given atoms is typically shorter than a single covalent bond. Studies of the $O_3$ and other similar molecules showed that the bonds were identical in length. Interestingly, the length of the bond is in between the lengths expected for an O–O single bond and a double bond.

**Resonance** is the use of two or more Lewis structures to represent the covalent bonding in a molecule. One of the valid structures is referred to as a resonance structure. It is now understood that the true structure of a molecule which displays resonance is that of an average or a hybrid of all the resonance structures. In the case of the $O_3$ molecule, each of the covalent bonds between O atoms are best thought of as being "one and a half" bonds, as opposed to either a pure single bond or a pure double bond. This "half-bond" can be shown as a dotted line in both the Lewis structure and the molecular model (Figure **4.6.2**).



Figure **4.6.2**: "Half-bond" model of ozone molecule. This is a better description of the electronic structure of ozone than either of the resonance structures in Figure **4.6.1**.

Many polyatomic ions also display resonance. In some cases, the true structure may be an average of three valid resonance structures, as in the case of the nitrate ion, $NO_3^-$ in Figure **4.6.3**.

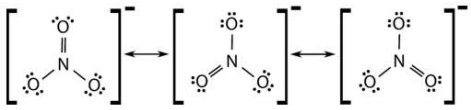


Figure **4.6.3**: Resonance structure of nitrate anion.

The bond lengths between the central N atom and each O atom are identical and the bonds can be approximated as being equal to one and one-third bonds.

## Summary

- Resonance structures are averages of different Lewis structure possibilities.
- Bond lengths are intermediate between covalent bonds and covalent double bonds.

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# 4.7: PREDICTING THE SHAPES OF MOLECULES

**LEARNING OBJECTIVE**

- Determine the shape of simple molecules.

We have considered the Lewis structures of covalent compounds, but these have been two-dimensional representations of a three-dimensional world. What do these compounds really look like, and how can we describe the shape and three-dimensional structure.

## VALENCE SHELL ELECTRON PAIR REPULSION

Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is called **valence shell electron pair repulsion (VSEPR).** VSEPR says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from one another as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include $BeH_2$ and $CO_2$:




Figure **4.7.1**: Beryllium hydride and carbon dioxide bonding.

The two molecules, shown in the figure below in a "ball and stick" model.

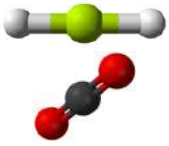


Figure **4.7.2**: Beryllium hydride and carbon dioxide models. (CK12 Licence)

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is $BF_3$:

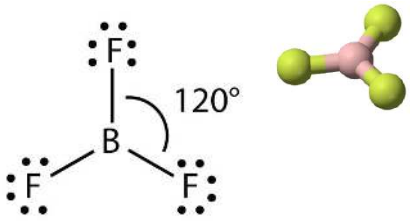



Figure **4.7.3**: Boron trifluoride bonding. (CK12 Licence)

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is $GeF_2$:

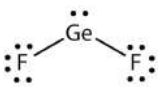



Figure **4.7.4**: Germanium difluoride bonding.

From an electron group geometry perspective, $GeF_2$ has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure **4.7.1** Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane ($CH_4$) is an example.

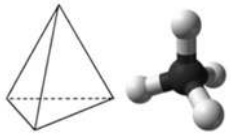


Figure **4.7.5**: Tetrahedral structure of methane. (CK12 Licence)

This diagram of $CH_4$ illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

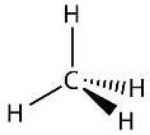



Figure **4.7.6**: Methane bonding. (CK12 Licence)

$NH_3$ is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.

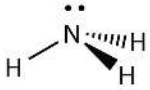



Figure **4.7.7**: Ammonia bonding. (CK12 Licence)

Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of $NH_3$ is *trigonal pyramidal*.

$H_2O$ is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.




Figure **4.7.8**: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom, is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde ($CH_2O$) is shown in Figure **4.7.9**.




Figure **4.7.9**: Lewis Electron Dot Diagram of Formaldehyde.

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape.

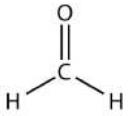



Figure **4.7.10**: Formaldehyde bonding.

(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

Table **4.7.1** summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table 4.7.1: Summary of Molecular Shapes

| Number of Electron Groups on Central Atom | Number of Bonding Groups | Number of Lone Pairs | Electron Geometry | Molecular Shape |
|---|---|---|---|---|
| 2 | 2 | 0 | linear | linear |
| 3 | 3 | 0 | trigonal planar | trigonal planar |
| 3 | 2 | 1 | trigonal planar | bent |
| 4 | 4 | 0 | tetrahedral | tetrahedral |
| 4 | 3 | 1 | tetrahedral | trigonal pyramidal |
| 4 | 2 | 2 | tetrahedral | bent |

## EXAMPLE 4.7.1

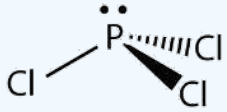
What is the approximate shape of each molecule?

a. $PCl_3$
b. NOF

### Solution

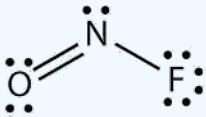
The first step is to draw the Lewis structure of the molecule.

For $PCl_3$, the electron dot diagram is as follows:




The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

The electron dot diagram for NOF is as follows:




The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

## EXERCISE 4.7.1

What is the approximate molecular shape of $CH_2Cl_2$?

**Answer**

Tetrahedral

## EXERCISE 4.7.2

Ethylene ($C_2H_4$) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule. (Hint: hydrogen is a terminal atom.)

**Answer**

Trigonal planar about both central C atoms.

## SUMMARY

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

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# 4.8: Electronegativity and Polarity - Why Oil and Water Do not Mix

**Learning Objectives**

- Explain how polar compounds differ from nonpolar compounds.
- Determine if a molecule is polar or nonpolar.
- Given a pair of compounds, predict which would have a higher melting or boiling point.

## Bond Polarity

The ability of an atom in a molecule to attract shared electrons is called **electronegativity**. When two atoms combine, the difference between their electronegativities is an indication of the type of bond that will form. If the difference between the electronegativities of the two atoms is small, neither atom can take the shared electrons completely away from the other atom, and the bond will be covalent. If the difference between the electronegativities is large, the more electronegative atom will take the bonding electrons completely away from the other atom (electron transfer will occur), and the bond will be ionic. This is why metals (low electronegativities) bonded with nonmetals (high electronegativities) typically produce ionic compounds.

A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity? Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure 4.8.1.

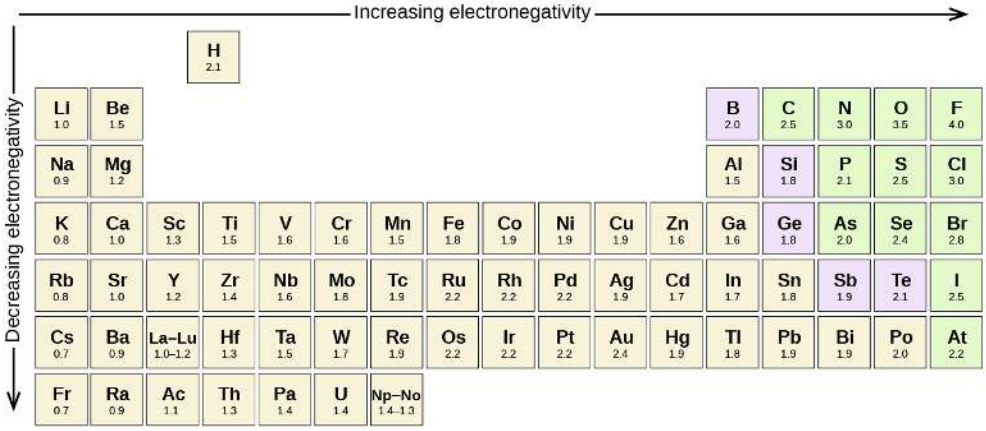



Figure 4.8.1: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

The polarity of a covalent bond can be judged by determining the *difference* of the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table:

difference of the electronegativities of the two atoms involved in the covalent bond

| Electronegativity Difference | Bond Type |
|---|---|
| 0–0.4 | pure covalent |
| 0.5–2.0 | polar covalent |
| >2.0 | likely ionic |

### Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.9 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

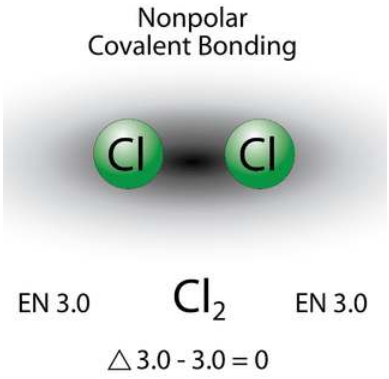



Figure **4.8.2**: A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the $Cl_2$ molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.5) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta EN = 3.0 - 2.8 = 0.2$).

## Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.5 and 2.0 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

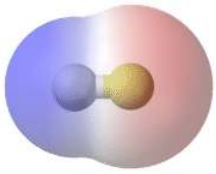


Figure **4.8.3**: In the polar covalent bond of **HF**, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta ($\delta$).

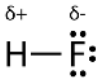



Figure **4.8.4**: Use of $\delta$ to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.




Figure **4.8.5**: Use of crossed arrow to indicate polarity.



*Electronegativity differences in bonding using Pauling scale. Differences in electronegativity classify bonds as covalent, polar covalent, or ionic.*

### Example 4.8.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

**Solution**

Using Figure **4.8.1**, we can calculate the difference of the electronegativities of the atoms involved in the bond.

a. For the C–H bond, the difference in the electronegativities is 2.5 − 2.1 = 0.4. Thus we predict that this bond will be nonpolar covalent.
b. For the O–H bond, the difference in electronegativities is 3.5 − 2.1 = 1.4, so we predict that this bond will be polar covalent.

### Exercise 4.8.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

**Answer a**

likely ionic

**Answer b**

polar covalent

## Molecular Polarity

To determine if a molecule is polar or nonpolar, it is generally useful to look at Lewis structures. **Nonpolar compounds** will be symmetric, meaning all of the sides around the central atom are identical—bonded to the same element with no unshared pairs of electrons. **Polar molecules** are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded. This works pretty well, as long as you can visualize the molecular geometry. That's the hard part. To know how the bonds are oriented in space, you have to have a strong grasp of Lewis structures and VSEPR theory. Assuming that you do, you can look at the structure of each one and decide if it is polar or not, *whether or not you know the individual atom's electronegativity*. This is because you know that all bonds between dissimilar elements are polar, and in these particular examples, it doesn't matter which direction the dipole moment vectors are pointing (out or in).

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as **HF**, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.




Figure 4.8.6: A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide ($CO_2$) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the **C** atom to each **O** atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out and the overall molecular polarity of $CO_2$ is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the **H** atoms toward the **O** atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

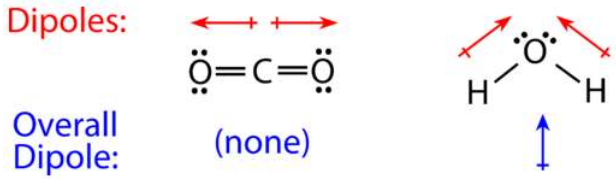



Figure 4.8.7: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as $CH_4$ is nonpolar. However, if one of the peripheral **H** atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule ($BF_3$) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule ($NH_3$) is polar.

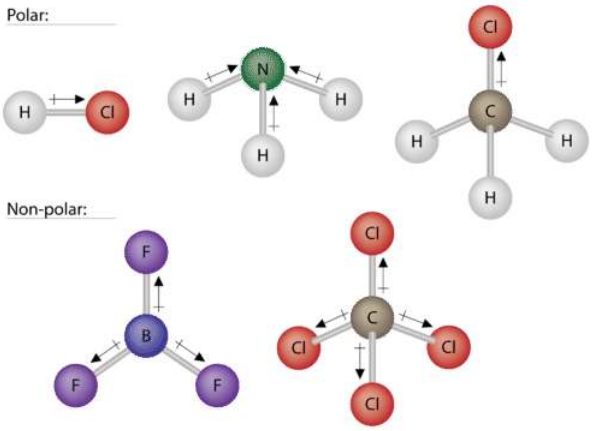



Figure 4.8.8: Some examples of polar and nonpolar molecules based on molecular geometry.

**To summarize, to be polar, a molecule must:**

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment do not cancel.

**Steps to Identify Polar Molecules**

1. Draw the Lewis structure.
2. Figure out the geometry (using VSEPR theory).
3. Visualize or draw the geometry.
4. Find the net dipole moment (you don't have to actually do calculations if you can visualize it).
5. If the net dipole moment is zero, it is non-polar. Otherwise, it is polar.

## Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure **4.8.14**). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

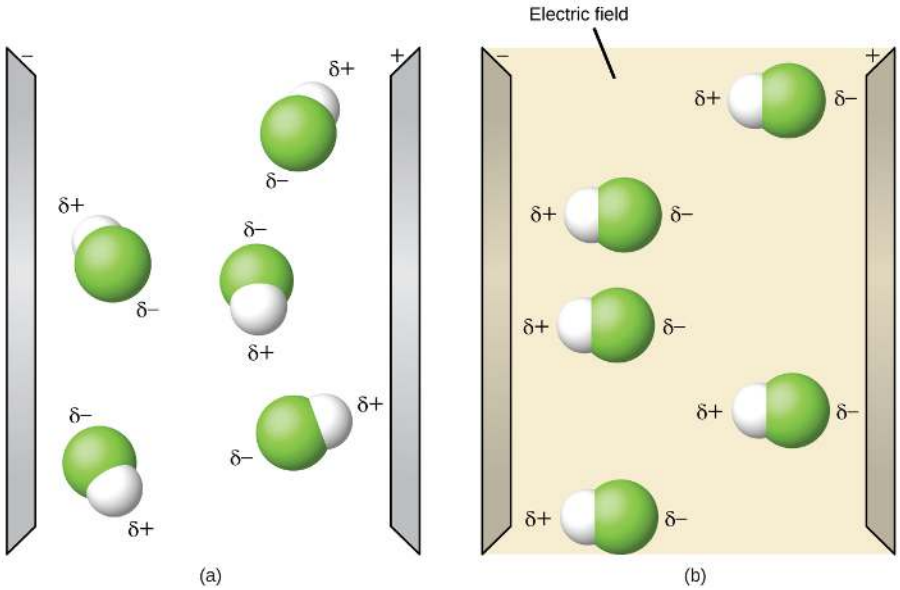



Figure **4.8.9**: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

While molecules can be described as "polar covalent" or "ionic", it must be noted that this is often a relative term, with one molecule simply being *more polar* or *less polar* than another. However, the following properties are typical of such molecules. Polar molecules tend to:

- have higher melting points than nonpolar molecules
- have higher boiling points than nonpolar molecules
- be more soluble in water (dissolve better) than nonpolar molecules
- have lower vapor pressures than nonpolar molecules

**Example 4.8.2:**

Label each of the following as polar or nonpolar.

a. Water, $H_2O$:

b. Methanol, $CH_3OH$:

c. Hydrogen Cyanide, HCN: H–C≡N

d. Oxygen, $O_2$:

e. Propane, $C_3H_8$: 

**Solution**

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.
b. Methanol is polar. This is not a symmetric molecule. The $-OH$ side is different from the other 3 $-H$ sides.
c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.
d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.
e. Propane is nonpolar, because it is symmetric, with $H$ atoms bonded to every side around the central atoms and no unshared pairs of electrons.

**? Exercise 4.8.2**

Label each of the following as polar or nonpolar.

a. $SO_3$
b. $NH_3$

**Answer a**

nonpolar

**Answer b**

polar

## Contributions & Attributions

- StackExchange (thomij).

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# CHAPTER OVERVIEW

## 5: Chemical Reactions


5.1: Prelude to Introduction to Chemical Reactions
5.2: The Mole
5.3: Atomic and Molar Masses
5.3.1: Gram-Mole Conversions
5.4: The Law of Conservation of Matter
5.5: Chemical Equations
5.5.1: How to Write Balanced Chemical Equations
5.6: Mole Relationships and Chemical Equations
5.7: Mass Relationships and Chemical Equations
5.8: Limiting Reagent and Percent Yield


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# 5.1: Prelude to Introduction to Chemical Reactions

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are single-celled fungi. About 1,000 species are recognized, but the most common species is *Saccharomyces cerevisiae*, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

Yeasts live primarily on sugars, such as glucose ($C_6H_{12}O_6$). They convert glucose into carbon dioxide ($CO_2$) and ethanol ($C_2H_5OH$) in a chemical transformation that is represented as follows:

$$C_6H_{12}O_6\,(s) \longrightarrow 2\,CO_2\,(g) + 2\,C_2H_5OH(\ell)$$

Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of yeast, fermentation, depends on the production of ethanol, which results from the same chemical transformation. Some alcoholic beverages, such as champagne, can also be carbonated using the carbon dioxide produced by the yeast.

Yeast is among the simplest life forms on Earth, yet it is absolutely necessary for at least two major food industries. Without yeast to turn dough into bread and juice into wine, these foods and food industries would not exist today.

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# 5.2: The Mole

**Learning Objectives**

- To define the mole unit.
- Perform conversions between moles, molecules, atoms, or ions.

Figure 5.2.1 shows that we need 2 hydrogen atoms and 1 oxygen atom to make 1 water molecule. If we want to make 2 water molecules, we will need 4 hydrogen atoms and 2 oxygen atoms. If we want to make 5 molecules of water, we need 10 hydrogen atoms and 5 oxygen atoms. The ratio of atoms we will need to make any number of water molecules is the same: 2 hydrogen atoms to 1 oxygen atom.

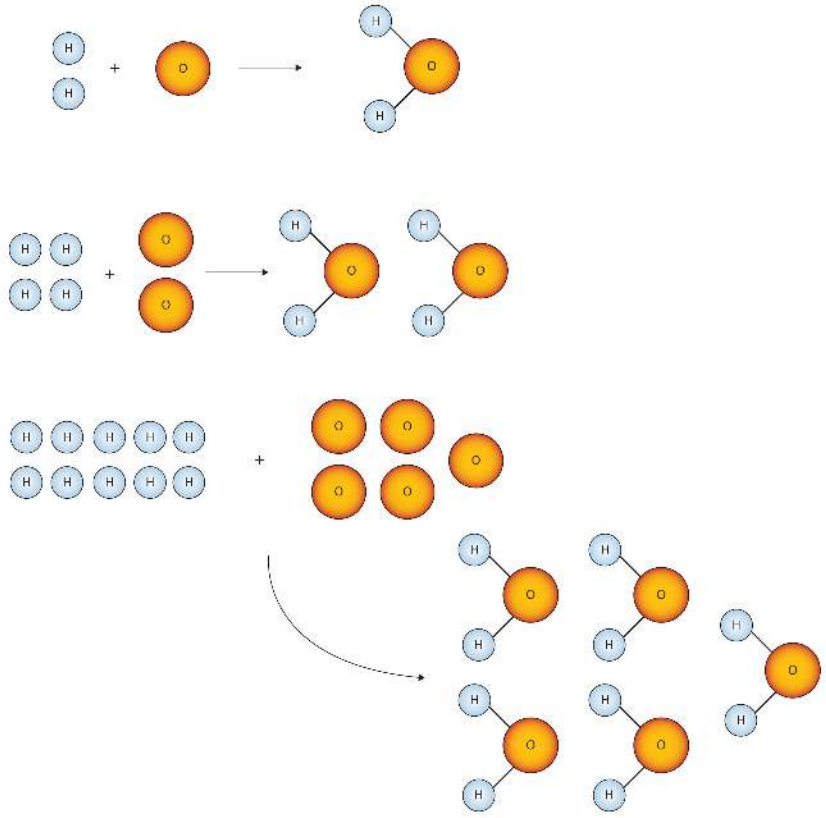


Figure 5.2.1 Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

One problem we have, however, is that it is extremely difficult, if not impossible, to organize atoms one at a time. As stated in the introduction, we deal with billions of atoms at a time. How can we keep track of so many atoms (and molecules) at a time? We do it by using mass rather than by counting individual atoms.

A hydrogen atom has a mass of approximately 1 u. An oxygen atom has a mass of approximately 16 u. The ratio of the mass of an oxygen atom to the mass of a hydrogen atom is therefore approximately 16:1.

If we have 2 atoms of each element, the ratio of their masses is approximately 32:2, which reduces to 16:1—the same ratio. If we have 12 atoms of each element, the ratio of their total masses is approximately (12 × 16):(12 × 1), or 192:12, which also reduces to 16:1. If we have 100 atoms of each element, the ratio of the masses is approximately 1,600:100, which again reduces to 16:1. As long as we have equal numbers of hydrogen and oxygen atoms, the ratio of the masses will always be 16:1.

The same consistency is seen when ratios of the masses of other elements are compared. For example, the ratio of the masses of silicon atoms to equal numbers of hydrogen atoms is always approximately 28:1, while the ratio of the masses of calcium atoms to equal numbers of lithium atoms is approximately 40:7.

So we have established that the masses of atoms are constant with respect to each other, as long as we have the same number of each type of atom. Consider a more macroscopic example. If a sample contains 40 g of Ca, this sample has the same number of atoms as there are in a sample of 7 g of Li. What we need, then, is a number that represents a convenient quantity of atoms so we can relate macroscopic quantities of substances. Clearly even 12 atoms are too few because atoms themselves are so small. We need a number that represents billions and billions of atoms.

## The Mole

Chemists use the term **mole** to represent a large number of atoms or molecules. Just as a dozen implies 12 things, a **mole** (abbreviated as ***mol***) represents **$6.022 \times 10^{23}$ things**. The number $6.022 \times 10^{23}$, called Avogadro's number after the 19th-century chemist Amedeo Avogadro, is the number we use in chemistry to represent macroscopic amounts of atoms and molecules. Thus, if we have $6.022 \times 10^{23}$ Na atoms, we say we have 1 mol of Na atoms. If we have 2 mol of Na atoms, we have $2 \times (6.022 \times 10^{23})$ Na atoms, or $1.2044 \times 10^{24}$ Na atoms. Similarly, if we have 0.5 mol of benzene ($C_6H_6$) molecules, we have $0.5 \times (6.022 \times 10^{23})$ $C_6H_6$ molecules, or $3.011 \times 10^{23}$ $C_6H_6$ molecules.

> A mole represents a very large number! If 1 mol of quarters were stacked in a column, it could stretch back and forth between Earth and the sun *6.8 billion* times.

Notice that we are applying the mole unit to different types of **chemical entities**. The word *mole* represents a number of things—$6.022 \times 10^{23}$ of them—but does not by itself specify what "they" are. The chemical entities can be ***atoms, molecules***, ***formula units*** and ***ions***. This specific information needs to be specified accurately. Most students find this confusing hence, we need to review the composition of elements, covalent and ionic compounds.

Most elements are made up of individual ***atoms,*** such as helium. However, some elements consist of ***molecules***, such as the diatomic elements, nitrogen, hydrogen, oxygen, etc. One mole of He consists of $6.022 \times 10^{23}$ He ***atoms*** but one mole of nitrogen contains $6.022 \times 10^{23}$ $N_2$ ***molecules***. The basic units of covalent (molecular) compounds are ***molecules*** as well. The molecules of "compounds" consist of different kinds of atoms while the molecules of "elements" consist of only one type of atom. For example, the molecules of ammonia ($NH_3$) consist of nitrogen and hydrogen atoms while $N_2$ molecules have N atoms only. Compounds that are ionic, like NaCl, are represented by ionic formulas. One mole of NaCl, for example, refers to $6.022 \times 10^{23}$ ***formula units*** of NaCl. And, one formula unit of NaCl consists of one sodium ***ion*** and one chloride ***ion***. Figure 6.1.2 summarizes the basic units of elements, covalent and ionic compounds

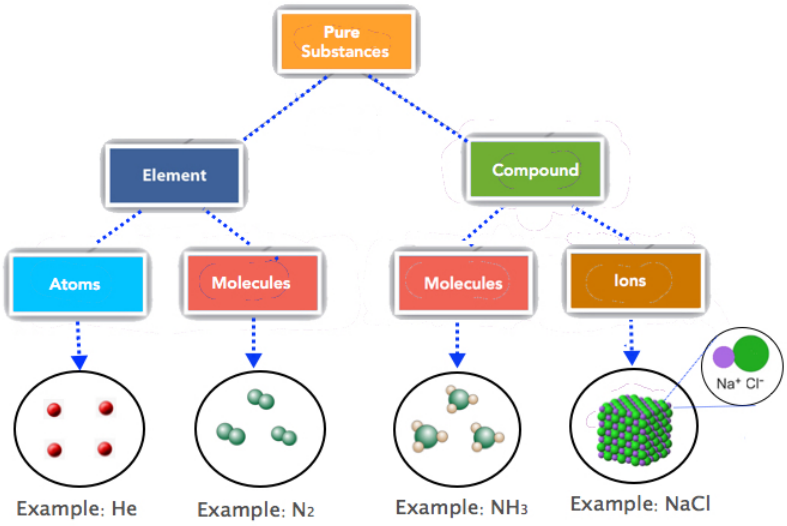



Figure **5.2.2**: The basic units of elements (atoms or molecules), covalent compounds (molecules) and ionic compounds (formula units of ions).

## Conversion Between Moles and Atoms, Molecules and Ions

Using our unit conversion techniques learned in Chapter 1, we can use the mole relationship and the chemical formula to convert back and forth between the moles and the number of chemical entities (atoms, molecules or ions).

Because 1 $N_2$ molecule contains 2 N atoms, 1 mol of $N_2$ molecules ($6.022 \times 10^{23}$ molecules) has 2 mol of N atoms. Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of ethanol ($C_2H_6O$), we can construct the following relationships (Table **5.2.1**):

Table **5.2.1**: Molecular Relationships

| 1 Molecule of $C_2H_6O$ Has | 1 Mol of $C_2H_6O$ Has | Molecular Relationships |
|---|---|---|
| 2 C atoms | 2 mol of C atoms | $\frac{\text{2 mol C atoms}}{\text{1 mol } C_2H_6O \text{ molecules}}$ or $\frac{\text{1 mol } C_2H_6O \text{ molecules}}{\text{2 mol C atoms}}$ |
| 6 H atoms | 6 mol of H atoms | $\frac{\text{6 mol H atoms}}{\text{1 mol } C_2H_6O \text{ molecules}}$ or $\frac{\text{1 mol } C_2H_6O \text{ molecules}}{\text{6 mol H atoms}}$ |
| 1 O atom | 1 mol of O atoms | $\frac{\text{1 mol O atoms}}{\text{1 mol } C_2H_6O \text{ molecules}}$ or $\frac{\text{1 mol } C_2H_6O \text{ molecules}}{\text{1 mol O atoms}}$ |

The following example illustrates how we can use these relationships as conversion factors.

### Example 5.2.1

If a sample consists of 2.5 mol of ethanol ($C_2H_6O$), how many moles of carbon atoms, hydrogen atoms, and oxygen atoms does it have?

**Solution**

Using the relationships in Table **5.2.1**, we apply the appropriate conversion factor for each element:

$$2.5 \text{ mol } C_2H_6O \text{ molecules} \times \underbrace{\frac{2 \text{ mol C atoms}}{1 \text{ mol } C_2H_6O \text{ molecules}}}_{\text{conversion factor}} = 5.0 \text{ mol C atoms}$$

Note how the unit *mol $C_2H_6O$ molecules* cancels algebraically. Similar equations can be constructed for determining the number of H and O atoms:

$$\text{2.5 mol } C_2H_6O \text{ molecules} \times \frac{\text{6 mol H atoms}}{\text{1 mol } C_2H_6O \text{ molecules}} = \text{15 mol H atoms}$$

$$\text{2.5 mol } C_2H_6O \text{ molecules} \times \frac{\text{1 mol O atoms}}{\text{1 mol } C_2H_6O \text{ molecules}} = \text{2.5 mol O atoms}$$

### Exercise 5.2.1

If a sample contains 6.75 mol of $Na_2SO_4$, how many moles of sodium atoms, sulfur atoms, and oxygen atoms does it have?

**Answer**

13.5 mol Na, 6.75 mol S and 27 mol O.

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. For example, if we are dealing with element X, the mole relationship is expressed as follows:

$$\text{1 mol X} = 6.022 \times 10^{23} \text{ X atoms}$$

We can convert this relationship into two possible conversion factors shown below:

$$\frac{1\ \text{mol X}}{6.022 \times 10^{23}\ \text{X atoms}} \text{ or } \frac{6.022 \times 10^{23}\ \text{X atoms}}{1\ \text{mol X}}$$

If the number of "atoms of element X" is given, we can convert it into "moles of X" by multiplying the given value with the conversion factor at the left. However, if the number of "mol of X" is given, the appropriate conversion factor to use is the one at the right.

If we are dealing with a molecular compound (such as $C_4H_{10}$), the mole relationship is expressed as follows:

$$1\ \text{mol C4H10} = 6.022 \times 10^{23}\ \text{C4H10 molecules}$$

If working with ionic compounds (such as NaCl), the mole relationship is expressed as follows:

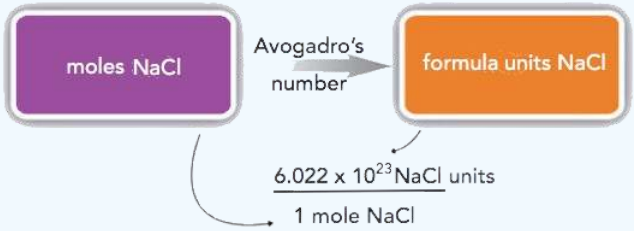
$$1\ \text{mol NaCl} = 6.022 \times 10^{23}\ \text{NaCl formula units}$$

## Example 5.2.2

How many formula units are present in 2.34 mol of NaCl? How many ions are in 2.34 mol?

### Solution

Typically in a problem like this, we start with what we are given and apply the appropriate conversion factor. Here, we are given a quantity of 2.34 mol of NaCl, to which we can apply the definition of a **mole as a conversion factor**:




$$2.34\ \text{mol NaCl} \times \frac{6.022 \times 10^{23}\ \text{NaCl units}}{1\ \text{mol NaCl}} = 1.41 \times 10^{24}\ \text{NaCl units}$$

Because there are two ions per formula unit, there are

$$1.41 \times 10^{24}\ \text{NaCl units} \times \frac{2\ \text{ions}}{\text{NaCl units}} = 2.82 \times 10^{24}\ \text{ions}$$

in the sample.

## Exercise 5.2.2

How many molecules are present in 16.02 mol of $C_4H_{10}$? How many atoms are in 16.02 mol?

### Answer

9.647 x $10^{24}$molecules, 1.351 x $10^{26}$ atoms.

## Key Takeaway

- A mole is $6.022 \times 10^{23}$ things.

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# 5.3: Atomic and Molar Masses

**Learning Objectives**

- Define molar mass.
- Calculate the molar mass of a atom, ion, or compound.

Now that we have introduced the mole and practiced using it as a conversion factor, we ask the obvious question: why is the mole *that particular* number of things? Why is it $6.022 \times 10^{23}$ and not $1 \times 10^{23}$ or even $1 \times 10^{20}$?

## Molar Mass

The number in a mole, Avogadro's number, is related to the relative sizes of the **atomic mass unit** and **gram mass units**. Whereas one hydrogen atom has a mass of approximately 1 u, **1 mol of H atoms** has a mass of approximately **1 *gram***. And whereas one sodium atom has an approximate mass of 23 u, 1 mol of Na atoms has an approximate mass of 23 *grams*.

*One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units.* The numbers in the periodic table that we identified as the atomic masses of the atoms not only tell us the mass of one atom in u but also tell us the mass of 1 mol of atoms in grams.

> One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units.

**Example 5.3.1: Moles to Mass Conversion with Elements**

What is the mass of each quantity?

a. 1 mol of Al atoms
b. 2 mol of U atoms

**Solution**

a. One mole of Al atoms has a mass in grams that is numerically equivalent to the atomic mass of aluminum. The periodic table shows that the atomic mass (rounded to two decimal points) of Al is 26.98, so 1 mol of Al atoms has a mass of 26.98 g.
b. According to the periodic table, 1 mol of U has a mass of 238.0 g, so the mass of 2 mol is twice that, or 476.0 g.

**Exercise 5.3.1: Moles to Mass Conversion with Elements**

What is the mass of each quantity?

a. 1 mol of Au atoms
b. 5 mol of Br atoms

**Answer a:**

197.0 g

**Answer b:**

5 mol Br atoms x 79.90 g/mol = 399.5 g

The mole concept can be extended to masses of formula units and molecules as well. The mass of 1 mol of molecules (or formula units) in grams is numerically equivalent to the mass of one molecule (or formula unit) in atomic mass units. For example, a single molecule of $O_2$ has a mass of 32.00 u, and 1 mol of $O_2$ molecules has a mass of 32.00 g. As with atomic mass unit–based masses, to obtain the mass of 1 mol of a substance, we simply sum the masses of the individual atoms in the formula of that substance. The

mass of 1 mol of a substance is referred to as its **molar mass**, whether the substance is an element, an ionic compound, or a covalent compound.

### Example 5.3.2: Moles to Mass Conversion with Compounds

What is the mass of 1 mol of each substance?

1. NaCl
2. bilirubin ($C_{33}H_{36}N_4O_6$), the principal pigment present in bile (a liver secretion)

**Solution**

1. Summing the molar masses of the atoms in the NaCl formula unit gives

| | |
|---|---|
| **1 Na molar mass:** | 22.99 g |
| **1 Cl molar mass:** | 35.45 g |
| **Total:** | 58.44 g |

The mass of 1 mol of NaCl is 58.44 g.

2. Multiplying the molar mass of each atom by the number of atoms of that type in bilirubin's formula and adding the results, we get

| | | |
|---|---|---|
| **33 C molar mass:** | 33 × 12.01 g | 396.33 g |
| **36 H molar mass:** | 36 × 1.01 = | 36.36 g |
| **4 N molar mass:** | 4 × 14.01 = | 56.04 g |
| **6 O molar mass:** | 6 × 16.00 = | 96.00 g |
| **Total:** | | 584.73 g |

The mass of 1 mol of bilirubin is 584.73 g.

### Exercise 5.3.2: Moles to Mass Conversion with Compounds

What is the mass of 1 mol of each substance?

a. barium sulfate ($BaSO_4$), used to take X rays of the gastrointestional tract
b. adenosine ($C_{10}H_{13}N_5O_4$), a component of cell nuclei crucial for cell division

**Answer a:**

233.36 g

**Answer b:**

267.28 g

Be careful when counting atoms. In formulas with polyatomic ions in parentheses, the subscript outside the parentheses is applied to every atom inside the parentheses. For example, the molar mass of $Ba(OH)_2$ requires the sum of 1 mass of Ba, 2 masses of O, and 2 masses of H:

| | | |
|---|---|---|
| **1 Ba molar mass:** | 1 × 137.3 g = | 137.3 g |
| **2 O molar mass:** | 2 × 16.00 g = | 32.00 g |
| **2 H molar mass:** | 2 × 1.01 g = | 2.02 g |
| **Total:** | | 171.32 g |

Because molar mass is defined as the mass for 1 mol of a substance, we can refer to molar mass as grams per mole (g/mol). The division sign (/) implies "per," and "1" is implied in the denominator. Thus, the molar mass of bilirubin can be expressed as 584.73 g/mol, which is read as "five hundred eighty four point seventy three grams per mole."

## Key Takeaway

- The mass of moles of atoms and molecules is expressed in units of grams.

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# 5.3.1: Gram-Mole Conversions

**Learning Objectives**

- To convert between mass units and mole units.

As we just discussed, **molar mass** is defined as the mass (in grams) of 1 mole of substance (or Avogadro's number of molecules or formula units).

## Molar Mass as a Conversion Factor

The simplest type of manipulation using molar mass as a *conversion factor* is a mole-gram conversion (or its reverse, a gram-mole conversion).

We also established that 1 mol of Al has a mass of 26.98 g (Example 5.3.1.1). Stated mathematically,

$$1 \text{ mol Al} = 26.98 \text{ g Al}$$

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \quad \text{and} \quad \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

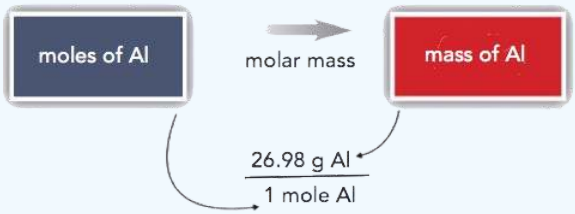
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

**5.3.1.1 Example**

What is the mass of 3.987 mol of Al?

**Solution**

The first step in a conversion problem is to decide what conversion factor to use. Because we are starting with mole units, we want a conversion factor that will cancel the mole unit and introduce the unit for mass in the numerator. Therefore, we should use the $\frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$ conversion factor. We start with the given quantity and multiply by the conversion factor:




$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

Note that the mol units cancel algebraically. (The quantity 3.987 mol is understood to be in the numerator of a fraction that has 1 in the unwritten denominator.) Canceling and solving gives

$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 107.6 \text{ g Al}$$

Our final answer is expressed to four significant figures.

**5.3.1.1 Exercise**

How many moles are present in 100.0 g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

**Answer**

$$100.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 3.706 \text{ mol Al}$$

## Gram-to-Mole Conversions

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure **5.3.1.1** is a chart for determining what conversion factor is needed, and Figure **5.3.1.2** is a flow diagram for the steps needed to perform a conversion.

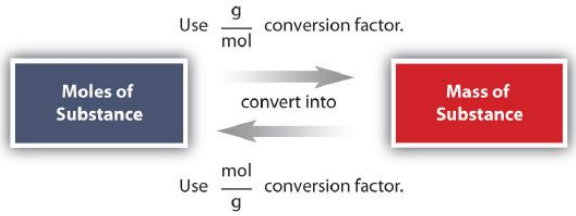



Figure **5.3.1.1** A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

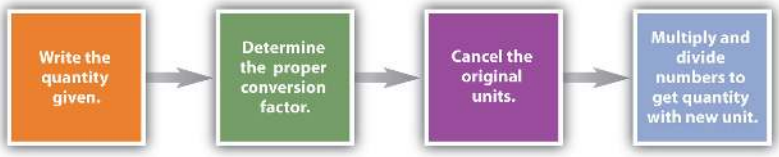



Figure **5.3.1.2** A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

### 5.3.1.2 Example

A biochemist needs 0.00655 mol of bilirubin ($C_{33}H_{36}N_4O_6$) for an experiment. How many grams of bilirubin will that be?

**Solution**

To convert from moles to mass, we need the molar mass of bilirubin, which we can determine from its chemical formula:

| | | |
|---|---|---|
| **33 C molar mass:** | 33 × 12.01 g = | 396.33 g |
| **36 H molar mass:** | 36 × 1.01 g = | 36.36 g |
| **4 N molar mass:** | 4 × 14.01 g = | 56.04 g |
| **6 O molar mass:** | 6 × 16.00 g = | 96.00 g |
| **Total:** | | 584.73 g |

The molar mass of bilirubin is 584.73 g. Using the relationship

$$1 \text{ mol bilirubin} = 584.73 \text{ g bilirubin}$$

we can construct the appropriate conversion factor for determining how many grams there are in 0.00655 mol. Following the steps from Figure **5.3.1.2**:

$$0.00655 \text{ mol bilirubin} \times \frac{584.73 \text{ g bilirubin}}{\text{mol bilirubin}} = 3.83 \text{ g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

### 5.3.1.2 Exercise

A chemist needs 457.8 g of $KMnO_4$ to make a solution. How many moles of $KMnO_4$ is that?

**Answer**

$$457.8 \text{ g } KMnO_4 \times \frac{1 \text{ mol } KMnO_4}{158.04 \text{ g } KMnO_4} = 2.897 \text{ mol } KMnO_4$$

## To Your Health: Minerals

For our bodies to function properly, we need to ingest certain substances from our diets. Among our dietary needs are minerals, the noncarbon elements our body uses for a variety of functions, such developing bone or ensuring proper nerve transmission. The US Department of Agriculture has established some recommendations for the RDIs of various minerals. The accompanying table lists the RDIs for minerals, both in mass and moles, assuming a 2,000-calorie daily diet.

Table **5.3.1.1**: Essential Minerals and their Composition in Humans

| Mineral | Male (age 19–30 y) | | Female (age 19–30 y) | |
|---|---|---|---|---|
| Ca | 1,000 mg | 0.025 mol | 1,000 mg | 0.025 mol |
| Cr | 35 µg | $6.7 \times 10^{-7}$ mol | 25 µg | $4.8 \times 10^{-7}$ mol |
| Cu | 900 µg | $1.4 \times 10^{-5}$ mol | 900 µg | $1.4 \times 10^{-5}$ mol |
| F | 4 mg | $2.1 \times 10^{-4}$ mol | 3 mg | $1.5 \times 10^{-4}$ mol |
| I | 150 µg | $1.2 \times 10^{-6}$ mol | 150 µg | $1.2 \times 10^{-6}$ mol |
| Fe | 8 mg | $1.4 \times 10^{-4}$ mol | 18 mg | $3.2 \times 10^{-4}$ mol |
| K | 3,500 mg | $9.0 \times 10^{-2}$ mol | 3,500 mg | $9.0 \times 10^{-2}$ mol |
| Mg | 400 mg | $1.6 \times 10^{-2}$ mol | 310 mg | $1.3 \times 10^{-2}$ mol |
| Mn | 2.3 mg | $4.2 \times 10^{-5}$ mol | 1.8 mg | $3.3 \times 10^{-5}$ mol |
| Mo | 45 mg | $4.7 \times 10^{-7}$ mol | 45 mg | $4.7 \times 10^{-7}$ mol |
| Na | 2,400 mg | $1.0 \times 10^{-1}$ mol | 2,400 mg | $1.0 \times 10^{-1}$ mol |
| P | 700 mg | $2.3 \times 10^{-2}$ mol | 700 mg | $2.3 \times 10^{-2}$ mol |
| Se | 55 µg | $7.0 \times 10^{-7}$ mol | 55 µg | $7.0 \times 10^{-7}$ mol |
| Zn | 11 mg | $1.7 \times 10^{-4}$ mol | 8 mg | $1.2 \times 10^{-4}$ mol |

Table **5.3.1.1** illustrates several things. First, the needs of men and women for some minerals are different. The extreme case is for iron; women need over twice as much as men do. In all other cases where there is a different RDI, men need more than women.

Second, the amounts of the various minerals needed on a daily basis vary widely—both on a mass scale and a molar scale. The average person needs 0.1 mol of Na a day, which is about 2.5 g. On the other hand, a person needs only about 25–35 µg of Cr per day, which is under one millionth of a mole. As small as this amount is, a deficiency of chromium in the diet can lead to diabetes-like symptoms or neurological problems, especially in the extremities (hands and feet). For some minerals, the body does not require much to keep itself operating properly.

Although a properly balanced diet will provide all the necessary minerals, some people take dietary supplements. However, too much of a good thing, even minerals, is not good. Exposure to too much chromium, for example, causes a skin irritation, and certain forms of chromium are known to cause cancer (as presented in the movie *Erin Brockovich*).

## Concept Review Exercises

1. What relationship is needed to perform mole-mass conversions?
2. What information determines which conversion factor is used in a mole-mass conversion?

## Answers

1. The atomic or molar mass is needed for a mole-mass conversion.
2. The unit of the initial quantity determines which conversion factor is used.

## Key Takeaway

- It is possible to convert between moles of material and mass of material.

## Exercises

1. What is the mass of 8.603 mol of Fe metal?
2. What is the mass of 0.552 mol of Ag metal?
3. What is the mass of $6.24 \times 10^4$ mol of $Cl_2$ gas?
4. What is the mass of 0.661 mol of $O_2$ gas?
5. What is the mass of 20.77 mol of $CaCO_3$?
6. What is the mass of $9.02 \times 10^{-3}$ mol of the hormone epinephrine ($C_9H_{13}NO_3$)?
7. How many moles are present in 977.4 g of $NaHCO_3$?
8. How many moles of erythromycin ($C_{37}H_{67}NO_{13}$), a widely used antibiotic, are in $1.00 \times 10^3$ g of the substance?
9. Cortisone ($C_{21}H_{28}O_5$) is a synthetic steroid that is used as an anti-inflammatory drug. How many moles of cortisone are present in one 10.0 mg tablet?
10. Recent research suggests that the daily ingestion of 85 mg of aspirin (also known as acetylsalicylic acid, $C_9H_8O_4$) will reduce a person's risk of heart disease. How many moles of aspirin is that?

## Answers

1. 480.5 g
2. 59.6 g
3. $4.42 \times 10^6$ g
4. 21.2 g
5. 2,079 g
6. 1.65 g
7. 11.63 mol
8. 1.36 mol
9. $2.77 \times 10^{-5}$ mol
10. $4.7 \times 10^{-4}$ mol

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# 5.4: The Law of Conservation of Matter

**Learning Objectives**

- Correctly define a law as it pertains to science.
- State the law of conservation of matter.

In science, a law is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge. One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It 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*.

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. These eventually formed the basis of Dalton's Atomic Theory of Matter.

## Law of Conservation of Mass

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.

$$\underbrace{\overbrace{\mathrm{HgO\,(s)}}^{\text{Mercuric oxide}}}_{100\ \mathrm{g}} \rightarrow \underbrace{\overbrace{\mathrm{Hg\,(l)}}^{\text{Mercury}}}_{92.6\ \mathrm{g}} + \underbrace{\overbrace{\mathrm{O_2\,(g)}}^{\text{Oxygen}}}_{7.4\ \mathrm{g}}$$

Another way of stating this is, "In a chemical reaction, matter is neither created nor destroyed." The law of conservation of mass is also known as the "law of indestructibility of matter."

**Example 5.4.1**

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



A sample of calcium carbonate (CaCO3). (Public Domain; Walkerma).

**Solution**

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

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

What does this mean for chemistry? In any chemical change, one or more initial substances change into a different substance or substances. Both the initial and final substances are composed of atoms because all matter is composed of atoms. According to the

law of conservation of matter, matter is neither created nor destroyed, so we must have the **same number and kind of atoms** after the chemical change as were present before the chemical change.

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Figure 5.1.1 shows that 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.

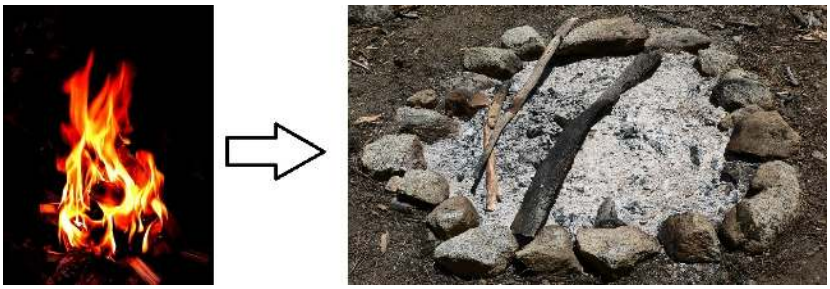


Figure 5.1.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

**? Exercise 5.4.1**

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.

## Key Takeaway

The amount of matter in a closed system is conserved.

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# 5.5: Chemical Equations

**Learning Objectives**

- Identify the reactants and products in any chemical reaction.
- Convert word equations into chemical equations.
- Use the common symbols, $(s)$, $(l)$, $(g)$, $(aq)$, and $\rightarrow$ appropriately when writing a chemical reaction.

In a chemical change, new substances are formed. In order for this to occur, the chemical bonds of the substances break, and the atoms that compose them separate and rearrange themselves into new substances with new chemical bonds. When this process occurs, we call it a chemical reaction. A **chemical reaction** is the process in which one or more substances are changed into one or more new substances.

## Reactants and Products

To describe a chemical reaction, we need to indicate what substances are present at the beginning and what substances are present at the end. The substances that are present at the beginning are called **reactants** and the substances present at the end are called **products**.

Sometimes when reactants are put into a reaction vessel, a reaction will take place to produce products. Reactants are the starting materials, that is, whatever we have as our initial ingredients. The products are just that—what is produced—or the result of what happens to the reactants when we put them together in the reaction vessel. If we think about baking chocolate chip cookies, our reactants would be flour, butter, sugar, vanilla, baking soda, salt, egg, and chocolate chips. What would be the products? Cookies! The reaction vessel would be our mixing bowl.

$$\underbrace{\text{Flour}+\text{Butter}+\text{Sugar}+\text{Vanilla}+\text{Baking Soda}+\text{Eggs}+\text{Chocolate Chips}}_{\text{Ingredients = Reactants}} \rightarrow \underbrace{\text{Cookies}}_{\text{Product}}$$

## Writing Chemical Equations

When sulfur dioxide is added to oxygen, sulfur trioxide is produced. Sulfur dioxide and oxygen, $SO_2 + O_2$, are reactants and sulfur trioxide, $SO_3$, is the product.

$$\underbrace{2\,SO_2\,(g)+O_2\,(g)}_{\text{Reactants}} \rightarrow \underbrace{2\,SO_3\,(g)}_{\text{Products}}$$

In chemical reactions, the reactants are found before the symbol "$\rightarrow$" and the products are found after the symbol "$\rightarrow$". The general equation for a reaction is:

$$\text{Reactants} \rightarrow \text{Products}$$

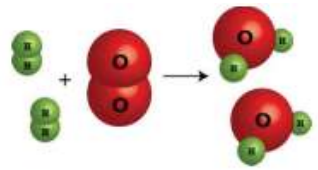
There are a few special symbols that we need to know in order to "talk" in chemical shorthand. In the table below is the summary of the major symbols used in chemical equations. Table 5.5.1 shows a listing of symbols used in chemical equations.

Table 5.5.1: Symbols Used in Chemical Equations

| Symbol | Description | Symbol | Description |
|---|---|---|---|
| $+$ | used to separate multiple reactants or products | $(s)$ | reactant or product in the solid state |
| $\rightarrow$ | yield sign; separates reactants from products | $(l)$ | reactant or product in the liquid state |
| $\rightleftharpoons$ | replaces the yield sign for reversible reactions that reach equilibrium | $(g)$ | reactant or product in the gas state |
| $\xrightarrow{\text{Pt}}$ | formula written above the arrow is used as a catalyst in the reaction | $(aq)$ | reactant or product in an aqueous solution (dissolved in water) |
| $\xrightarrow{\Delta}$ | triangle indicates that the reaction is being heated | | |

Chemists have a choice of methods for describing a chemical reaction.

1. They could draw a picture of the chemical reaction.



2. They could write a word equation for the chemical reaction:
*"Two molecules of hydrogen gas react with one molecule of oxygen gas to produce two molecules of water vapor."*

3. They could write the equation in chemical shorthand.

$$2\text{H}_2\,(g) + \text{O}_2\,(g) \rightarrow 2\text{H}_2\text{O}\,(g)$$

In the symbolic equation, chemical formulas are used instead of chemical names for reactants and products, while symbols are used to indicate the phase of each substance. It should be apparent that the chemical shorthand method is the quickest and clearest method for writing chemical equations.

We could write that an aqueous solution of calcium nitrate is added to an aqueous solution of sodium hydroxide to produce solid calcium hydroxide and an aqueous solution of sodium nitrate. Or in shorthand we could write:

$$\text{Ca(NO}_3)_2\,(aq) + 2\text{NaOH}\,(aq) \rightarrow \text{Ca(OH)}_2\,(s) + 2\text{NaNO}_3\,(aq)$$

How much easier is that to read? Let's try it in reverse. Look at the following reaction in shorthand and write the word equation for the reaction:

$$\text{Cu}\,(s) + \text{AgNO}_3\,(aq) \rightarrow \text{Cu(NO}_3)_2\,(aq) + \text{Ag}\,(s)$$

The word equation for this reaction might read something like "solid copper reacts with an aqueous solution of silver nitrate to produce a solution of copper (II) nitrate with solid silver."

To turn word equations into symbolic equations, we need to follow the given steps:

1. Identify the reactants and products. This will help you know which symbols go on each side of the arrow and where the $+$ signs go.
2. Write the correct formulas for all compounds. You will need to use the rules you learned in Chapter 5 (including making all ionic compounds charge balanced).

3. Write the correct formulas for all elements. Usually this is given straight off of the periodic table. However, there are seven elements that are considered diatomic, meaning that they are always found in pairs in nature. They include those elements listed in the table.

Table **5.5.1**: *Diatomic Elements*

| **Element Name** | Hydrogen | Nitrogen | Oxygen | Fluorine | Chlorine | Bromine | Iodine |
|---|---|---|---|---|---|---|---|
| **Formula** | $H_2$ | $N_2$ | $O_2$ | $F_2$ | $Cl_2$ | $Br_2$ | $I_2$ |

## Example 5.5.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. $\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$

b. Gaseous propane, $\mathrm{C_3H_8}$, burns in oxygen gas to produce gaseous carbon dioxide and liquid water.

c. Hydrogen fluoride gas reacts with an aqueous solution of potassium carbonate to produce an aqueous solution of potassium fluoride, liquid water, and gaseous carbon dioxide.

### Solution

a. An aqueous solution of hydrochloric acid reacts with an aqueous solution of sodium hydroxide to produce an aqueous solution of sodium chloride and liquid water.

b. Reactants: propane ($\mathrm{C_3H_8}$) and oxygen ($\mathrm{O_2}$)

Product: carbon dioxide ($\mathrm{CO_2}$) and water ($\mathrm{H_2O}$)

$$\mathrm{C_3H_8}\,(g) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

c. Reactants: hydrogen fluoride and potassium carbonate

Products: potassium fluoride, water, and carbon dioxide

$$\mathrm{HF}\,(g) + \mathrm{K_2CO_3}\,(aq) \rightarrow \mathrm{KF}\,(aq) + \mathrm{H_2O}\,(l) + \mathrm{CO_2}\,(g)$$

## Exercise 5.5.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. Hydrogen gas reacts with nitrogen gas to produce gaseous ammonia.

b. $\mathrm{HCl}\,(aq) + \mathrm{LiOH}\,(aq) \rightarrow \mathrm{LiCl}\,(aq) + \mathrm{H_2O}\,(l)$

c. Copper metal is heated with oxygen gas to produce solid copper(II) oxide.

**Answer a**

$H_2(g) + N_2(g) \rightarrow NH_3(g)$

**Answer b**

An aqueous solution of hydrochloric acid reacts with an aqueous solution of lithium hydroxide to produce an aqueous solution of lithium chloride and liquid water.

**Answer c**

$Cu(s) + O_2(g) \rightarrow CuO(s)$

## Summary

- A chemical reaction is the process by which one or more substances are changed into one or more new substances.
- Chemical reactions are represented by chemical equations.
- Chemical equations have reactants on the left, an arrow that is read as "yields", and the products on the right.

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# 5.5.1: How to Write Balanced Chemical Equations

**Learning Objectives**

- Explain the roles of subscripts and coefficients in chemical equations.
- Balance a chemical equation when given the unbalanced equation.
- Explain the role of the Law of Conservation of Mass in a chemical reaction.

Even though chemical compounds are broken up and new compounds are formed during a chemical reaction, atoms in the reactants do not disappear, nor do new atoms appear to form the products. In chemical reactions, atoms are never created or destroyed. The same atoms that were present in the reactants are present in the products—they are merely reorganized into different arrangements. In a complete chemical equation, the two sides of the equation must be present on the reactant and the product sides of the equation.

## Coefficients and Subscripts

There are two types of numbers that appear in chemical equations. There are subscripts, which are part of the chemical formulas of the reactants and products; and there are coefficients that are placed in front of the formulas to indicate how many molecules of that substance is used or produced.

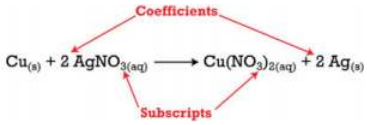
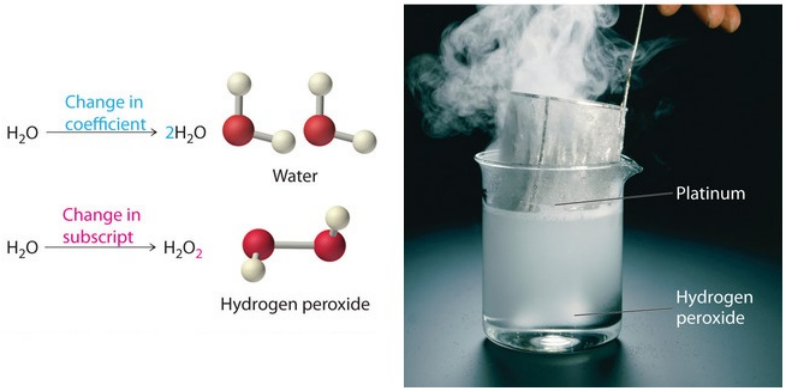



Figure 5.5.1.1: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water ($H_2O$) and hydrogen 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.

The **subscripts** are part of the formulas and once the formulas for the reactants and products are determined, the subscripts may not be changed. The **coefficients** indicate the number of each substance involved in the reaction and may be changed in order to balance the equation. The equation above indicates that one mole of solid copper is reacting with two moles of aqueous silver nitrate to produce one mole of aqueous copper (II) nitrate and two atoms of solid silver.

## Balancing a Chemical 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 5.5.1.1.




Original molecule $H_2O$: if the coefficient 2 is added in front, that makes 2 water molecules; but if the subscript 2 is added to make $H_2O_2$, that's hydrogen peroxide.

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(s) that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element(s) on both sides.
3. Balance polyatomic ions (if present on both sides of the chemical equation) 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. Count the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

### Example 5.5.1.1: Combustion of Heptane

Balance the chemical equation for the combustion of Heptane ($C_7H_{16}$).

$$C_7H_{16}\,(l) + O_2\,(g) \longrightarrow CO_2\,(g) + H_2O\,(g)$$

**Solution**

Solutions to Example 5.5.1.1

| Steps | 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.** | a. 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:<br>$$C_7H_{16}(l) + O_2(g) \longrightarrow \underline{7}CO_2(g) + H_2O(g)$$<br>• 7 carbon atoms on both reactant and product sides<br>b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 $H_2O$ molecules, each of which contains 2 hydrogen atoms, on the right side:<br>$$C_7H_{16}(l) + O_2(g) \longrightarrow 7\,CO_2(g) + \underline{8}H_2O(g)$$<br>• 16 hydrogen atoms on both reactant and product sides |
| 3. **Balance polyatomic ions as a unit.** | There are no polyatomic ions to be considered in this reaction. |
| 4. **Balance the remaining atoms.** | 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:<br>$$C_7H_{16}(l) + \underline{11}O_2(g) \longrightarrow 7\,CO_2(g) + 8\,H_2O(g)$$<br>• 22 oxygen atoms on both reactant and product sides |
| 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. |

### ✔ Example 5.5.1.2: Combustion of Isooctane

Combustion of Isooctane ($C_8H_{18}$)

$$C_8H_{18}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$

#### Solution

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. The combustion of any hydrocarbon with oxygen produces carbon dioxide and water.

Solutions to Example 7.4.2

| Steps | Example |
|---|---|
| 1. **Identify the most complex substance.** | The most complex substance is the one with the largest number of different atoms, which is $C_8H_{18}$. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance. |
| 2. **Adjust the coefficients.** | a. 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:<br>$$C_8H_{18}(l) + O_2(g) \longrightarrow \underline{8}CO_2(g) + H_2O(g)$$<br>• 8 carbon atoms on both reactant and product sides<br>b. 18 hydrogen atoms in isooctane means that there must be 9 $H_2O$ molecules in the products:<br>$$C_8H_{18}(l) + O_2(g) \longrightarrow 8\,CO_2(g) + \underline{9}H_2O(g)$$<br>• 18 hydrogen atoms on both reactant and product sides |
| 3. **Balance polyatomic ions as a unit.** | There are no polyatomic ions to be considered in this reaction. |
| 4. **Balance the remaining atoms.** | 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 ($\frac{25}{2}$) to balance the oxygen atoms:<br>$$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$$<br>• 25 oxygen atoms on both reactant and product sides<br>The equation 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**:<br>$$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$ |
| 5. **Check your work.** | The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side.<br>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 5.5.1.3: Precipitation of Lead (II) Chloride

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

**Solution**

Solutions to Example 7.4.3

| Steps | Example |
|---|---|
| 1. **Identify the most complex substance.** | The most complex substance is lead (II) chloride.<br>$Pb(NO_3)_2\,(aq) + NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)$ |
| 2. **Adjust the coefficients.** | There are twice as many chloride ions in the reactants as there are in the products. Place a 2 in front of the NaCl in order to balance the chloride ions.<br>$Pb(NO_3)_2\,(aq) + \underline{2}$<br>$NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)$<br>• 1 Pb atom on both reactant and product sides<br>• 2 Na atoms on reactant side, 1 Na atom on product side<br>• 2 Cl atoms on both reactant and product sides |
| 3. **Balance polyatomic ions as a unit.** | The nitrate ions are still unbalanced. Place a 2 in front of the $NaNO_3$. The result is:<br>$Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow \underline{2}$<br>$NaNO_3\,(aq) + PbCl_2\,(s)$<br>• 1 Pb atom on both reactant and product sides<br>• 2 Na atoms on both reactant and product sides<br>• 2 Cl atoms on both reactant and product sides<br>• 2 $NO_3^-$ atoms on both reactant and product sides |
| 4. **Balance the remaining atoms.** | There is no need to balance the remaining atoms because they are already balanced. |
| 5. **Check your work.** | $Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow 2\,NaNO_3\,(aq) + PbCl_2\,(s)$<br>• 1 Pb atom on both reactant and product sides<br>• 2 Na atoms on both reactant and product sides<br>• 2 Cl atoms on both reactant and product sides<br>• 2 $NO_3^-$ atoms on both reactant and product sides |

## ? Exercise 5.5.1.1

Is each chemical equation balanced?

a. $2\,Hg(\ell)^+\ O_2\,(g)\ \rightarrow Hg_2O_2\,(s)$
b. $C_2H_4\,(g) + 2\,O_2(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(g)$
c. $Mg(NO_3)_2\,(s) + 2\,Li\,(s)\ \rightarrow Mg(s)^+\ 2\,LiNO_3\,(s)$

**Answer a**

yes

**Answer b**

no

**Answer c**

yes

**? Exercise 5.5.1.2**

Balance the following chemical equations.

a. $\mathbf{N_2\,(g) + O_2\,(g) \longrightarrow NO_2\,(g)}$
b. $\mathbf{Pb(NO_3)_2\,(aq) + FeCl_3\,(aq) \longrightarrow Fe(NO_3)_3\,(aq) + PbCl_2\,(s)}$
c. $\mathbf{C_6H_{14}\,(l) + O_2(g) \longrightarrow CO_2\,(g) + H_2O\,(g)}$

**Answer a**

$N_2\,(g) + 2O_2\,(g) \rightarrow 2NO_2\,(g)$

**Answer b**

$3Pb(NO_3)_2(aq) + 2FeCl_3(aq) \rightarrow 2Fe(NO_3)_3(aq) + 3PbCl_2(s)$

**Answer c**

$2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$

## Summary

- To be useful, chemical equations must always be balanced. Balanced chemical equations have the same number and type of each atom on both sides of the equation.
- The coefficients in a balanced equation must be the simplest whole number ratio. Mass is always conserved in chemical reactions.

## Vocabulary

- **Chemical reaction** - The process in which one or more substances are changed into one or more new substances.
- **Reactants** - The starting materials in a reaction.
- **Products** - Materials present at the end of a reaction.
- **Balanced chemical equation** - A chemical equation in which the number of each type of atom is equal on the two sides of the equation.
- **Subscripts** - Part of the chemical formulas of the reactants and products that indicate the number of atoms of the preceding element.
- **Coefficient** - A small whole number that appears in front of a formula in a balanced chemical equation.

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# 5.6: Mole Relationships and Chemical Equations

**Learning Objectives**

- To use a balanced chemical reaction to determine molar relationships between the substances.

Previously, you learned to balance chemical equations by comparing the numbers of each type of atom in the reactants and products. The coefficients in front of the chemical formulas represent the numbers of molecules or formula units (depending on the type of substance). Here, we will extend the meaning of the coefficients in a chemical equation.

## Stoichiometric Relationstips

Consider the simple chemical equation

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4\,H_2 + 2\,O_2 \longrightarrow 4\,H_2O$$

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22\,H_2 + 11\,O_2 \longrightarrow 22\,H_2O$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$

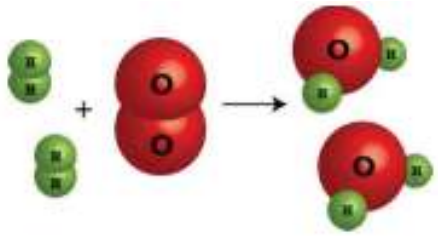
These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But $6.022 \times 10^{23}$ is 1 mol, while $12.044 \times 10^{23}$ is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ \text{mol}\ \ H_2 + 1\ \ \text{mol}\ \ O_2 \longrightarrow 2\ \text{mol}\ \ H_2O$$

We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level but also in terms of molar amounts of reactants and products.* Thus, we can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.”



2 molecules $H_2$ 1 molecule $O_2$ 2 molecules $H_2O$

2 moles $H_2$ 1 mole $O_2$ 2 moles $H_2O$

2 x 2.02 g=4.04 g $H_2$ 32.0 g $O_2$ 2 x 18.02 g=36.04 g $H_2O$

Figure 5.6.1: This representation of the production of water from oxygen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

By the same token, the ratios we constructed to describe molecules reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

$$\frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ O_2}\ \text{or}\ \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2}$$

$$\frac{2\ \text{mol}\ H_2O}{1\ \text{mol}\ O_2}\ \text{or}\ \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2O}$$

$$\frac{2\ \text{mol}\ H_2}{2\ \text{mol}\ H_2O}\ \text{or}\ \frac{2\ \text{mol}\ H_2O}{2\ \text{mol}\ H_2}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called ***stoichiometry***. The ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products is called the **stoichiometric factor.**

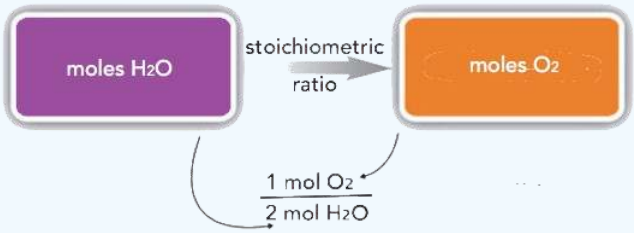
### Example 5.6.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of $H_2O$? The balanced equation is as follows:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

#### Solution

Because we are dealing with quantities of $H_2O$ and $O_2$, we will use the **stoichiometric ratio** that relates those two substances. Because we are given an amount of $H_2O$ and want to determine an amount of $O_2$, we will use the ratio that has $H_2O$ in the denominator (so it cancels) and $O_2$ in the numerator (so it is introduced in the answer). Thus,




$$27.6\ \text{mol}\ H_2O \times \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2O} = 13.8\ \text{mol}\ O_2$$

To produce 27.6 mol of $H_2O$, 13.8 mol of $O_2$ react.

### Exercise 5.6.1

Using $2H_2 + O_2 \rightarrow 2H_2O$, how many moles of hydrogen react with 3.07 mol of oxygen to produce $H_2O$?

**Answer**

$$3.07\ \text{mol}\ O_2 \times \frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ O_2} = 6.14\ \text{mol}\ H_2$$

## Key Takeaway

- The balanced chemical reaction can be used to determine molar relationships between substances.

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# 5.7: Mass Relationships and Chemical Equations

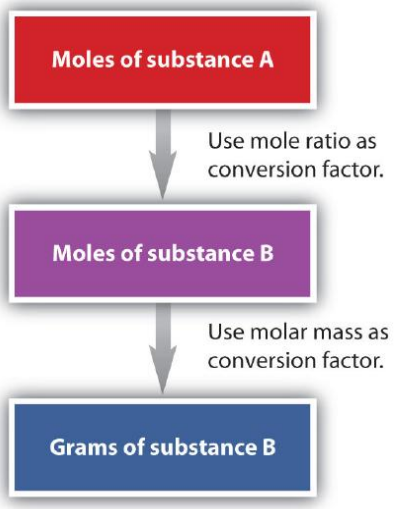
**Learning Objectives**

- To convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B.

## Conversions Involving Moles and Grams

We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:




Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

$$\mathrm{Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3}$$

If we have 3.59 mol of $Fe_2O_3$, how many grams of $SO_3$ can react with it? Using the mole-mass calculation sequence, we can determine the required mass of $SO_3$ in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of $SO_3$ needed. Then using the molar mass of $SO_3$ as a conversion factor, we determine the mass that this number of moles of $SO_3$ has.

The first step resembles the exercises we did in Section 6.4. As usual, we start with the quantity we were given:

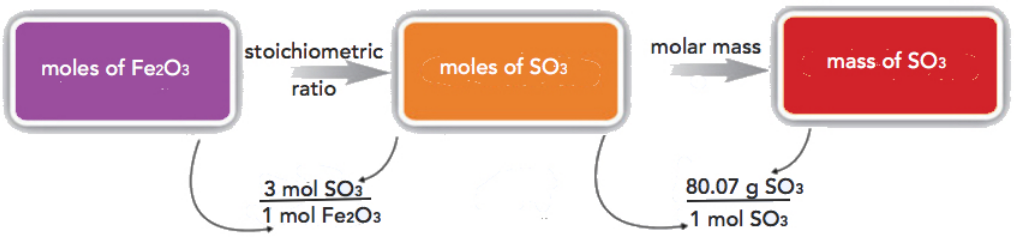
$$\mathrm{3.59\ mol\ Fe_2O_3 \times \frac{3\ mol\ SO_3}{1\ mol\ Fe_2O_3} = 10.77\ mol\ SO_3}$$

The mol $Fe_2O_3$ units cancel, leaving mol $SO_3$ unit. Now, we take this answer and convert it to grams of $SO_3$, using the molar mass of $SO_3$ as the conversion factor:

$$\mathrm{10.77\ mol\ SO_3 \times \frac{80.07\ g\ SO_3}{1\ mol\ SO_3} = 862.4\ g\ SO_3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of $SO_3$ will react with 3.59 mol of $Fe_2O_3$. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:




$$3.59 \text{ mol } Fe_2O_3 \times \underbrace{\frac{3 \text{ mol } SO_3}{1 \text{ mol } Fe_2O_3}}_{\text{converts to moles of } SO_3} \times \underbrace{\frac{80.07 \text{ g } SO_3}{1 \text{ mol } SO_3}}_{\text{converts to grams of } SO_3} = 862.4 \text{ g } SO_3$$

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

### Example 5.7.1

How many grams of $CO_2$ are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation?

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

**Solution**

Our strategy will be to convert from moles of HCl to moles of $CO_2$ and then from moles of $CO_2$ to grams of $CO_2$. We will need the molar mass of $CO_2$, which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of $CO_2$:

$$2.09 \text{ mol HCl} \times \underbrace{\frac{1 \text{ mol } CO_2}{2 \text{ mol HCl}}}_{\text{from the coefficients of the balanced equation}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 46.0 \text{ g } CO_2$$

The molar ratio between $CO_2$ and HCl comes from the balanced chemical equation.

### Exercise

How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of $H_2O$ are reacted according to this balanced chemical equation?

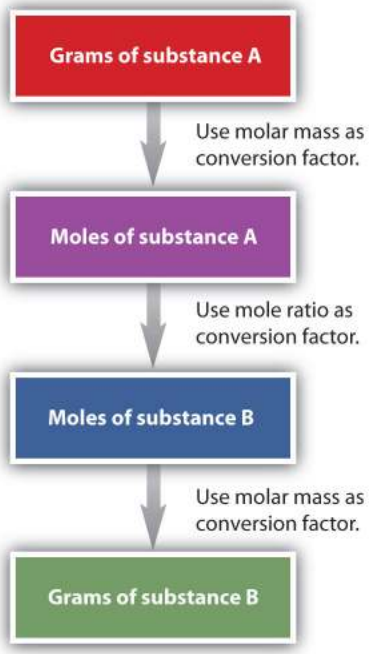
$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2$$

**Answer**

$$17.3 \text{ mol } H_2O \times \frac{1 \text{ mol } C_6H_{12}O_6}{6 \text{ mol } H_2O} \times \frac{180.18 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6} = 520 \text{ g } C_6H_{12}O_6$$

## Conversions Involving Grams

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:




This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques.

### Example 5.7.2: Chlorination of Carbon

Methane can react with elemental chlorine to make carbon tetrachloride ($CCl_4$). The balanced chemical equation is as follows:

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

How many grams of HCl are produced by the reaction of 100.0 g of $CCl_4$?

#### Solution

First, let us work the problem in stepwise fashion. We begin by converting the mass of $CCl_4$ to moles of $CCl_4$, using the molar mass of $CCl_4$ (16.05 g/mol) as the conversion factor:

$$100.0\ g\ CH_4 \times \frac{1\ mol\ CH_4}{16.05\ g\ CH_4} = 6.231\ mol\ CH_4$$

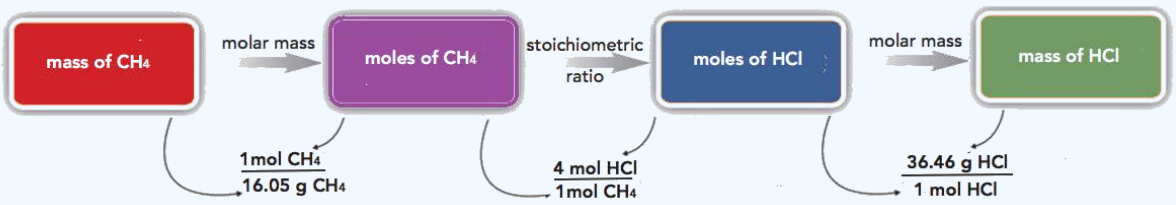
Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles $CCl_4$ and moles HCl and convert our first result into moles of HCl:

$$6.231\ mol\ CH_4 \times \frac{4\ mol\ HCl}{1\ mol\ CH_4} = 24.92\ mol\ HCl$$

Finally, we use the molar mass of HCl (36.46 g/mol) as a conversion factor to calculate the mass of 24.92 mol of HCl:

$$24.92\ mol\ HCl \times \frac{36.46\ g\ HCl}{1\ mol\ HCl} = 908.5\ g\ HCl$$

In each step, we have limited the answer to the proper number of significant figures. If desired, we can do all three conversions on a single line:



$$100.0\ \text{g CH}_4 \times \frac{1\ \text{mol CH}_4}{16.05\ \text{g CH}_4} \times \frac{4\ \text{mol HCl}}{1\ \text{mol CH}_4} \times \frac{36.46\ \text{g HCl}}{1\ \text{mol HCl}} = 908.7\ \text{g HCl}$$

This final answer is slightly different from our first answer because only the final answer is restricted to the proper number of significant figures. In the first answer, we limited each intermediate quantity to the proper number of significant figures. As you can see, both answers are essentially the same.

### ? Exercise 5.7.2: Oxidation of Propanal

The oxidation of propanal ($CH_3CH_2CHO$) to propionic acid ($CH_3CH_2COOH$) has the following chemical equation:

$$CH_3CH_2CHO + 2K_2Cr_2O_7 \rightarrow CH_3CH_2COOH + \text{other products}$$

How many grams of propionic acid are produced by the reaction of 135.8 g of $K_2Cr_2O_7$?

**Answer**

$$135.8\ \text{g K}_2\text{Cr}_2\text{O}_7 \times \frac{1\ \text{mol K}_2\text{Cr}_2\text{O}_7}{294.20\ \text{g K}_2\text{Cr}_2\text{O}_7} \times \frac{1\ \text{mol CH}_3\text{CH}_2\text{COOH}}{2\ \text{mol K}_2\text{Cr}_2\text{O}_7} \times \frac{74.09\ \text{g CH}_3\text{CH}_2\text{COOH}}{1\ \text{mol CH}_3\text{CH}_2\text{COOH}} = 17.10\ \text{g CH}_3\text{CH}_2\text{COOH}$$

### To Your Health: The Synthesis of Taxol

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

After a 20-year effort, two research groups announced the complete laboratory synthesis of taxol in 1994. However, each synthesis required over 30 separate chemical reactions, with an overall efficiency of less than 0.05%. To put this in perspective, to obtain a single 300 mg dose of taxol, you would have to begin with 600 g of starting material. To treat the 26,000 women who are diagnosed with ovarian cancer each year with one dose, almost 16,000 kg (over 17 tons) of starting material must be converted to taxol. Taxol is also used to treat breast cancer, with which 200,000 women in the United States are diagnosed every year. This only increases the amount of starting material needed.

Clearly, there is intense interest in increasing the overall efficiency of the taxol synthesis. An improved synthesis not only will be easier but also will produce less waste materials, which will allow more people to take advantage of this potentially life-saving drug.

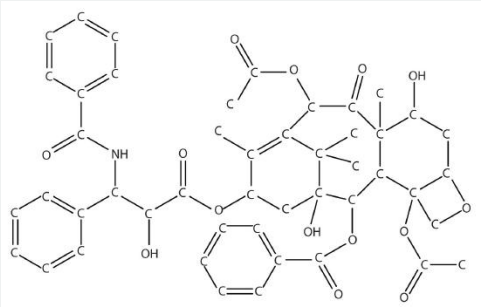



Figure 5.7.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

## Key Takeaway

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

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# 5.8: Limiting Reagent and Percent Yield

**Learning Objectives**

- Define and determine theoretical yields, actual yields, and percent yields.
- Identify a limiting reagent from a set of reactants.
- Calculate how much product will be produced from the limiting reagent.
- Calculate how much reactant(s) remains when the reaction is complete.

## Yield

In all the previous calculations we have performed involving balanced chemical equations, we made two assumptions:

1. The reaction goes exactly as written.
2. The reaction proceeds completely.

In reality, such things as side reactions occur that make some chemical reactions rather messy. For example, in the actual combustion of some carbon-containing compounds, such as methane, some CO is produced as well as $CO_2$. However, we will continue to ignore side reactions, unless otherwise noted. The second assumption, that the reaction proceeds completely, is more troublesome. Many chemical reactions do not proceed to completion as written, for a variety of reasons. When we calculate an amount of product assuming that all the reactant reacts, we calculate the **theoretical yield**, an amount that is theoretically produced as calculated using the balanced chemical reaction.

In many cases, however, this is not what really happens. In many cases, less—sometimes, much less—of a product is made during the course of a chemical reaction. The amount that is actually produced in a reaction is called the **actual yield**. By definition, the actual yield is less than or equal to the theoretical yield. If it is not, then an error has been made.

Both theoretical yields and actual yields are expressed in units of moles or grams. It is also common to see something called a percent yield. The **percent yield** is a comparison between the actual yield and the theoretical yield and is defined as

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{5.8.1}$$

It does not matter whether the actual and theoretical yields are expressed in moles or grams, as long as they are expressed in the same units. However, the percent yield always has units of percent. Proper percent yields are between 0% and 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.

**Example 5.8.1:**

A worker reacts 30.5 g of Zn with nitric acid and evaporates the remaining water to obtain 65.2 g of $Zn(NO_3)_2$. What are the theoretical yield, the actual yield, and the percent yield?

$$\mathrm{Zn\,(s) + 2\,HNO_3\,(aq) \longrightarrow Zn(NO_3)_2\,(aq) + H_2\,(g)}$$

**Solution**

A mass-mass calculation can be performed to determine the theoretical yield. We need the molar masses of Zn (65.39 g/mol) and $Zn(NO_3)_2$ (189.41 g/mol). In three steps, the mass-mass calculation is:

$$30.5\ \cancel{g\ Zn} \times \frac{1\ \cancel{mol\ Zn}}{65.39\ \cancel{g\ Zn}} \times \frac{1\ \cancel{mol\ Zn(NO_3)_2}}{1\ \cancel{mol\ Zn}} \times \frac{189.41\ g\ Zn(NO_3)_2}{1\ \cancel{mol\ Zn(NO_3)_2}} = 88.3\ g\ Zn(NO_3)_2$$

Thus, the theoretical yield is 88.3 g of $Zn(NO_3)_2$. The actual yield is the amount that was actually made, which was 65.2 g of $Zn(NO_3)_2$. To calculate the percent yield, we take the actual yield and divide it by the theoretical yield and multiply by 100 (Equation 5.8.1):

$$\frac{65.2\ g\ Zn(NO_3)_2}{88.3\ g\ Zn(NO_3)_2} \times 100\% = 73.8\%$$

The worker achieved almost three-fourths of the possible yield.

## ? Exercise 5.8.1

A synthesis produced 2.05 g of $NH_3$ from 16.5 g of $N_2$. What is the theoretical yield and the percent yield?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

*Technically, this is a reversible reaction (with double arrows), but for this exercise consider it irreversible (single arrow).

***Answer***

theoretical yield = 20.1 g; percent yield = 10.2%

## Chemistry is Everywhere: Actual Yields in Drug Synthesis and Purification

Many drugs are the product of several steps of chemical synthesis. Each step typically occurs with less than 100% yield, so the overall percent yield might be very small. The general rule is that the overall percent yield is the product of the percent yields of the individual synthesis steps. For a drug synthesis that has many steps, the overall percent yield can be very tiny, which is one factor in the huge cost of some drugs. For example, if a 10-step synthesis has a percent yield of 90% for each step, the overall yield for the entire synthesis is only 35%. Many scientists work every day trying to improve percent yields of the steps in the synthesis to decrease costs, improve profits, and minimize waste.

Even purifications of complex molecules into drug-quality purity are subject to percent yields. Consider the purification of impure albuterol. Albuterol ($C_{13}H_{21}NO_2$; accompanying figure) is an inhaled drug used to treat asthma, bronchitis, and other obstructive pulmonary diseases. It is synthesized from norepinephrine, a naturally occurring hormone and neurotransmitter. Its initial synthesis makes very impure albuterol that is purified in five chemical steps. The details of the steps do not concern us; only the percent yields do:

| | |
|---|---|
| impure albuterol → intermediate A | percent yield = 70% |
| intermediate A → intermediate B | percent yield = 100% |
| intermediate B → intermediate C | percent yield = 40% |
| intermediate C → intermediate D | percent yield = 72% |
| intermediate D → purified albuterol | percent yield = 35% |
| overall percent yield = 70% × 100% × 40% × 72% × 35% = 7.5% | |

That is, only about *one-fourteenth* of the original material was turned into the purified drug. This demonstrates one reason why some drugs are so expensive—a lot of material is lost in making a high-purity pharmaceutical.



Figure 5.8.1 A child using an albuterol inhaler, the container of albuterol medication, and a molecular model of the albuterol molecule. Source: Photo on far left © Thinkstock. Photo in center courtesy of Intropin, http://commons.wikimedia.org/wiki/Fi...te_%281%29.JPG.

## Limiting Reagent

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

$$\text{1 box mix} + \text{2 eggs} \rightarrow \text{1 batch brownies} \tag{5.8.2}$$

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.

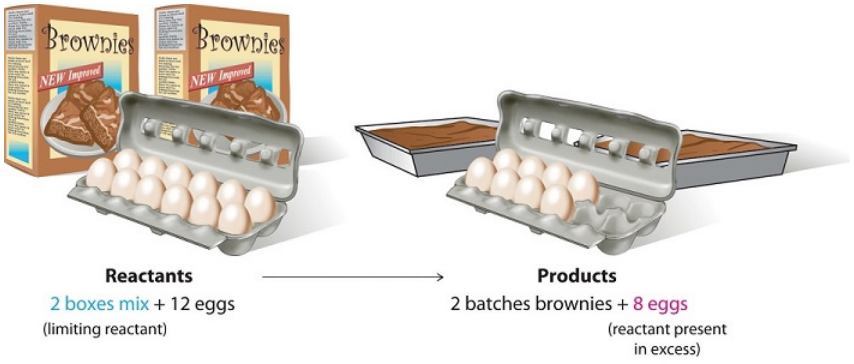



***Figure* 5.8.1**: *The Concept of a Limiting Reactant in the Preparation of Brownies*

A similar situation exists for many chemical reactions: you usually run out of one reactant before all of the other reactant has reacted. The reactant you run out of is called the **limiting reagent**; the other reactant or reactants are considered to be *in excess*. A crucial skill in evaluating the conditions of a chemical process is to determine which reactant is the limiting reagent and which is in excess.

The key to recognizing which reactant is the limiting reagent is based on a mole-mass or mass-mass calculation: whichever reactant gives the *lesser* amount of product is the limiting reagent. What we need to do is determine an amount of one product (either moles or mass), assuming all of each reactant reacts. Whichever reactant gives the least amount of that particular product is the limiting reagent. It does not matter which product we use, as long as we use the same one each time. It does not matter whether we

determine the number of moles or grams of that product; however, we will see shortly that knowing the final mass of product can be useful.

For example, consider this reaction:

$$4As(s) + 3O_2(g) \rightarrow 2As_2O_3(s)$$

Suppose we start a reaction with 50.0 g of As and 50.0 g of $O_2$. Which one is the limiting reagent? We need to perform two mole-mass calculations, each assuming that each reactant reacts completely. Then we compare the amount of the product produced by each and determine which is less.

The calculations are as follows:

$$50.0\ \cancel{g\ As} \times \frac{1\ \cancel{mol\ As}}{74.92\ \cancel{g\ As}} \times \frac{2\ mol\ As_2O_3}{4\ \cancel{mol\ As}} = 0.334\ mol\ As_2O_3$$

$$50.0\ \cancel{g\ O_2} \times \frac{1\ \cancel{mol\ O_2}}{32.00\ \cancel{g\ O_2}} \times \frac{2\ mol\ As_2O_3}{3\ \cancel{mol\ O_2}} = 1.04\ mol\ As_2O_3$$

Comparing these two answers, it is clear that 0.334 mol of $As_2O_3$ is less than 1.04 mol of $As_2O_3$, so arsenic is the limiting reagent. If this reaction is performed under these initial conditions, the arsenic will run out before the oxygen runs out. We say that the oxygen is "in excess."

Identifying the limiting reagent, then, is straightforward. However, there are usually two associated questions: (1) what mass of product (or products) is then actually formed? and (2) what mass of what reactant is left over? The first question is straightforward to answer: simply perform a conversion from the number of moles of product formed to its mass, using its molar mass. For $As_2O_3$, the molar mass is 197.84 g/mol; knowing that we will form 0.334 mol of $As_2O_3$ under the given conditions, we will get

$$0.334\ \cancel{mol\ As_2O_3} \times \frac{197.84\ g\ As_2}{1\ \cancel{mol\ As_2O_3}} = 66.1\ g\ As_2O_3$$

The second question is somewhat more convoluted to answer. First, we must do a mass-mass calculation relating the limiting reagent (here, As) to the other reagent ($O_2$). Once we determine the mass of $O_2$ that reacted, we subtract that from the original amount to determine the amount left over. According to the mass-mass calculation,

$$50.0\ \cancel{g\ As} \times \frac{1\ \cancel{mol\ As}}{74.92\ \cancel{g\ As}} \times \frac{3\ \cancel{mol\ O_2}}{4\ \cancel{mol\ As}} \times \frac{32.00\ g\ O_2}{1\ \cancel{mol\ O_2}} = 16.0\ g\ O_2\ reacted$$

Because we reacted 16.0 g of our original $O_2$, we subtract that from the original amount, 50.0 g, to get the mass of $O_2$ remaining:

50.0 g $O_2$ − 16.0 g $O_2$ reacted = 34.0 g $O_2$ left over

You must remember to perform this final subtraction to determine the amount remaining; a common error is to report the 16.0 g as the amount remaining.

**Example 5.8.1:**

A 5.00 g quantity of Rb is combined with 3.44 g of $MgCl_2$ according to this chemical reaction:

$$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$

What mass of Mg is formed, and what mass of what reactant is left over?

### Solution

Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations and determine which amount is less.

$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ Mg}}{2\ \cancel{mol\ Rb}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.711\ g\ Mg$$

$$3.44\ g\ MgCl_2 \times \frac{1\ mol\ MgCl_2}{95.21\ g\ MgCl_2} \times \frac{1\ mol\ Mg}{1\ mol\ MgCl_2} \times \frac{24.31\ g\ Mg}{1\ mol\ Mg} = 0.878\ g\ Mg$$

The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reagent. To determine how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass of MgCl2 reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount.

$$5.00\ g\ Rb \times \frac{1\ mol\ Rb}{85.47\ g\ Rb} \times \frac{1\ mol\ MgCl_2}{2\ mol\ Rb} \times \frac{95.21\ g\ Mg}{1\ mol\ MgCl_2} = 2.78\ g\ MgCl_2\ \ reacted$$

Because we started with 3.44 g of MgCl2, we have

3.44 g MgCl2 − 2.78 g MgCl2 reacted = 0.66 g MgCl2 left

**? Exercise 5.8.1**

Given the initial amounts listed, what is the limiting reagent, and what is the mass of the leftover reagent?

$$\underbrace{22.7\ g}_{MgO(s)} + \underbrace{17.9\ g}_{H_2S} \rightarrow MgS(s) + H_2O(l)$$

**Answer**

$H_2S$ is the limiting reagent; 1.5 g of MgO are left over.

## Summary

Theoretical yield is the calculated yield using the balanced chemical reaction. Actual yield is what is actually obtained in a chemical reaction. Percent yield is a comparison of the actual yield with the theoretical yield.

The limiting reagent is the reactant that produces the least amount of product. Mass-mass calculations can determine how much product is produced and how much of the other reactants remain.

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# CHAPTER OVERVIEW

## 6: Types of Chemical Reactions


6.1: Classifying Chemical Reactions

6.2: Aqueous Solutions and Solubility - Compounds Dissolved in Water

6.3: Precipitation Reactions

6.4: Oxidation–Reduction Reactions

6.5: Acids, Bases, and Neutralization Reactions


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# 6.1: Classifying Chemical Reactions

**Learning Objectives**

- Classify a chemical reaction as a synthesis, decomposition, single replacement, double replacement, or a combustion reaction.
- Predict the products of simple reactions.

The chemical reactions we have described are only a tiny sampling of the infinite number of chemical reactions possible. How do chemists cope with this overwhelming diversity? How do they predict which compounds will react with one another and what products will be formed? The key to success is to find useful ways to categorize reactions. Familiarity with a few basic types of reactions will help you to predict the products that form when certain kinds of compounds or elements come in contact.

Most chemical reactions can be classified into one or more of five basic types: acid–base reactions, exchange reactions, condensation reactions (and the reverse, cleavage reactions), and oxidation–reduction reactions. The general forms of these five kinds of reactions are summarized in Table **6.1.1**, along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion.

Table **6.1.1:** *Basic Types of Chemical Reactions*

| Name of Reaction | General Form | Examples |
|---|---|---|
| **Oxidation–Reduction (redox)** | oxidant + reductant → reduced oxidant + oxidized reductant | $C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(g)$ |
| **Acid–Base** | acid + base → salt | $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$ |
| **Exchange: Single Replacement** | AB + C → AC + B | $ZnCl_2(aq) + Mg(s) \rightarrow MgCl_2(aq) + Zn(s)$ |
| **Exchange: Double Replacement** | AB + CD → AD + CB | $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$ |
| **Combination (Synthesis)** | A + B → AB | $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$<br>$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ |
| **Decomposition** | AB → A + B | $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ |

The classification scheme is only for convenience; the same reaction can be classified in different ways, depending on which of its characteristics is most important. Oxidation–reduction reactions, in which there is a net transfer of electrons from one atom to another, and condensation reactions are discussed in this section. Acid–base reactions are one kind of exchange reaction—the formation of an insoluble salt, such as barium sulfate, when solutions of two soluble salts are mixed together.

## Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

$$\mathbf{A + B \rightarrow AB}$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

$$\mathbf{2Na\,(\mathit{s}) + Cl_2\,(\mathit{g}) \rightarrow 2NaCl\,(\mathit{s})}$$

Notice that in order to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules ($\mathbf{H_2}$, $\mathbf{N_2}$, $\mathbf{O_2}$, $\mathbf{F_2}$, $\mathbf{Cl_2}$, $\mathbf{Br_2}$, and $\mathbf{I_2}$).

One type of combination reaction that occurs frequently is the reaction of an element with oxygen to form an oxide. Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide:

$$2Mg\,(s) + O_2\,(g) \rightarrow 2MgO\,(s)$$

Sulfur reacts with oxygen to form sulfur dioxide:

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g)$$

When nonmetals react with one another, the product is a molecular compound. Often, the nonmetal reactants can combine in different ratios and produce different products. Sulfur can also combine with oxygen to form sulfur trioxide:

$$2S\,(s) + 3O_2\,(g) \rightarrow 2SO_3\,(g)$$

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron (II) oxide and iron (III) oxide:

$$2Fe\,(s) + O_2\,(g) \rightarrow 2FeO\,(s)$$

$$4Fe\,(s) + 3O_2\,(g) \rightarrow 2Fe_2O_3\,(s)$$

### Example 6.1.1: Combustion of Solid Potassium

Potassium is a very reactive alkali metal that must be stored under oil in order to prevent it from reacting with air. Write the balanced chemical equation for the combination reaction of potassium with oxygen.

#### Solution

Solutions to Example 7.10.1

| Steps | Example Solution |
|---|---|
| Plan the problem. | Make sure formulas of all reactants and products are correct before balancing the equation. Oxygen gas is a diatomic molecule. Potassium oxide is an ionic compound and so its formula is constructed by the crisscross method. Potassium as an ion becomes $K^+$, while the oxide ion is $O^{2-}$. |
| Solve. | The skeleton (unbalanced) equation: $$K\,(s) + O_2\,(g) \rightarrow K_2O\,(s)$$ The equation is then easily balanced with coefficients. $$4K\,(s) + O_2\,(g) \rightarrow 2K_2O\,(s)$$ |
| Think about your result. | Formulas are correct and the resulting combination reaction is balanced. |

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:

$$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g)$$

Two compounds may also react to form a more complex compound. A very common example is the reactions of oxides with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide:

$$CaO\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(aq)$$

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain.

$$SO_3\,(g) + H_2O\,(l) \rightarrow H_2SO_4\,(aq)$$




Figure **6.1.1**: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

**? Exercise 6.1.1**

a. Write the chemical equation for the synthesis of silver bromide, **AgBr**.
b. Predict the products for the following reaction: $CO_2\,(g) + H_2O\,(l)$

**Answer a:**

$2Ag + Br_2 \rightarrow 2AgBr$

**Answer b:**

$CO_2\,(g) + H_2O\,(l) \rightarrow H_2CO_3$

## Decomposition Reactions

A **decomposition reaction** is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

$$AB \rightarrow A + B$$

Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements. Mercury (II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas:

$$2HgO\,(s) \rightarrow 2Hg\,(l) + O_2\,(g)$$



***Video* 6.1.2*:*** *Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.*

A reaction is also considered to be a decomposition reaction even when one or more of the products are still compounds. A metal carbonate decomposes into a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes into calcium oxide and carbon dioxide:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water:

$$2NaOH\,(s) \rightarrow Na_2O\,(s) + H_2O\,(g)$$

Some unstable acids decompose to produce nonmetal oxides and water. Carbonic acid decomposes easily at room temperature into carbon dioxide and water:

$$H_2CO_3\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l)$$

### Example 6.1.2: Electrolysis of Water

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

**Solution**

Solutions to Example 7.10.2

| Steps | Example Solution |
|---|---|
| Plan the problem. | Water is a binary compound composed of hydrogen and oxygen. The hydrogen and oxygen gases produced in the reaction are both diatomic molecules. |
| Solve. | The skeleton (unbalanced) equation: $$H_2O\,(l) \xrightarrow{elec} H_2\,(g) + O_2\,(g)$$ Note the abbreviation "**elec**" above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation. $$2H_2O\,(l) \xrightarrow{elec} 2H_2\,(g) + O_2\,(g)$$ |
| Think about your result. | The products are elements and the equation is balanced. |

### Exercise 6.1.2

Write the chemical equation for the decomposition of:

a. $Al_2O_3$
b. $Ag_2S$

**Answer a**

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

**Answer b**

$$Ag_2S \rightarrow 2Ag + S$$

## Single Replacement Reactions

A third type of reaction is the single replacement reaction, in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B$$

In this general reaction, element **A** is a metal and replaces element **B**, also a metal, in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$\mathbf{Y + XZ \rightarrow XY + Z}$$

where **Y** is a nonmetal and replaces the nonmetal **Z** in the compound with **X**.

### Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$\mathrm{Mg\,(\mathit{s})} + \mathrm{Cu(NO_3)_2\,(\mathit{aq})} \rightarrow \mathrm{Mg(NO_3)_2\,(\mathit{aq})} + \mathrm{Cu\,(\mathit{s})}$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

### Hydrogen Replacement

Many metals react easily with acids and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

$$\mathrm{Zn\,(\mathit{s})} + \mathrm{2HCl\,(\mathit{aq})} \rightarrow \mathrm{ZnCl_2\,(\mathit{aq})} + \mathrm{H_2\,(\mathit{g})}$$

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal. Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All Group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see figure below).

$$\mathrm{2Na\,(\mathit{s})} + \mathrm{2H_2O\,(\mathit{l})} \rightarrow \mathrm{2NaOH\,(\mathit{aq})} + \mathrm{H_2\,(\mathit{g})}$$



Figure **6.1.2**: (First image) Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Second image) Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite.

### Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

$$\mathrm{Cl_2\,(\mathit{g})} + \mathrm{2NaBr\,(\mathit{aq})} \rightarrow \mathrm{2NaCl\,(\mathit{aq})} + \mathrm{Br_2\,(\mathit{l})}$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

**Example 6.1.3**

What are the products of the reaction between solid aluminum (**Al**) and iron (III) oxide ($\mathbf{Fe_2O_3}$)?

**Solution**

Solutions to Example 7.10.3

| Steps | Example Solution |
|---|---|
| Plan the problem. | To predict the products, we need to know that aluminum will replace iron and form aluminum oxide (the metal will replace the metal ion in the compound). Aluminum has a charge of $+3$ and oxygen has a charge of $-2$. The compound formed between aluminum and oxygen, therefore, will be $Al_2O_3$. Since iron is replaced in the compound by aluminum, the iron will now be the single element in the products. |
| Solve. | The unbalanced equation will be: $$Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe$$ and the balanced equation will be: $$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$ |
| Think about your result. | This is a single replacement reaction, and when balanced the coefficients accurately reflect that the iron and aluminum have the same charge in this reaction. |

**? Exercise 6.1.3**

a. Write the chemical equation for the single replacement reaction between zinc solid and lead (II) nitrate solution to produce zinc nitrate solution and solid lead. (Note that zinc forms ions with a $+2$ charge.)

b. Predict the products for the following reaction: $Fe + CuSO_4$. (In this reaction, assume iron forms ions with a $+2$ charge.)

**Answer a**

$$Zn + Pb(NO_3)_2 \rightarrow Pb + Zn(NO_3)_2$$

**Answer b**

$$Fe + CuSO_4 \rightarrow Cu + FeSO_4$$

## Double Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$AB + CD \rightarrow AD + BC$$

In this reaction, $A$ and $C$ are positively-charged cations, while $B$ and $D$ are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

### Formation of a Precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs:

$$2KI\,(aq) + Pb(NO_3)_2\,(aq) \rightarrow 2KNO_3\,(aq) + PbI_2\,(s) \qquad (6.1.1)$$

There are very strong attractive forces that occur between $Pb^{2+}$ and $I^-$ ions and the result is a brilliant yellow precipitate (Figure **6.1.3**). The other product of the reaction, potassium nitrate, remains soluble.



Figure **6.1.3**: Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate (Equation 6.1.1). (CC BY-SA 3.0; PRHaney).

### Formation of a Gas

Some double-replacement reactions produce a gaseous product which then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas:

$$\mathrm{Na_2S}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{H_2S}\,(g)$$

### Formation of a Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride and water:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

**Example 6.1.4**

Write a complete and balanced chemical equation for the double-replacement reaction $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed).

**Solution**

Solutions to Example 7.10.4

| Steps | Example Solution |
|---|---|
| Plan the problem. | The production of a gas drives the reaction. |
| Solve. | The cations of both reactants are $+1$ charged ions, while the anions are $-1$ charged ions. After exchanging partners, the balanced equation is: $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g)$ |
| Think about your result. | This is a double replacement reaction. All formulas are correct and the equation is balanced. |

**Exercise 6.1.4**

Write a complete and balanced chemical equation for the double-replacement reaction $(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms).

**Answer a:**

$$(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s)$$

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water:

$$\mathrm{Na_2CO_3}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\ \text{DEL}\ \mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

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# 6.2: Aqueous Solutions and Solubility - Compounds Dissolved in Water

**Learning Objectives**

- Define and recognize aqueous.
- Use solubility rules to predict the solubility of a compound.

Many of the reactions we encounter take place in water. We refer to these reactions as aqueous-phase reactions. But what happens when things dissolve in water?

## Aqueous Phase

When a solid dissolves in water, the solid structure breaks apart, yielding individual dissolves particles. We will take a closer look at what happens when solids dissolve in water in later sections, but here, we want to take a quick look at ionic compounds dissolved in water.

Water and other polar molecules are attracted to ions, as shown in Figure **6.2.1**. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

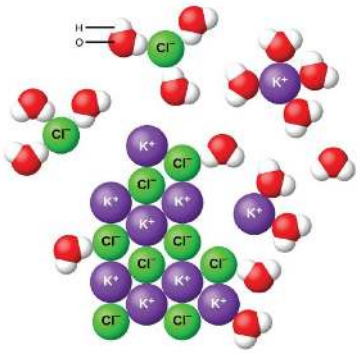



Figure **6.2.1**: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the $K^+$ and $Cl^-$ ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus and eight green spheres labeled C l superscript minus mixed and touching near the center of the diagram. Outside of this cluster of spheres are seventeen clusters of three spheres, which include one red and two white spheres. A red sphere in one of these clusters is labeled O. A white sphere is labeled H. Two of the green C l superscript minus spheres are surrounded by three of the red and white clusters, with the red spheres closer to the green spheres than the white spheres. One of the K superscript plus purple spheres is surrounded by four of the red and white clusters. The white spheres of these clusters are closest to the purple spheres.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual $K^+$ and $Cl^-$ ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure **6.2.1** shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system, as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions,

and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

## Solubility Rules

Some combinations of aqueous reactants result in the formation of a solid precipitate as a product. However, some combinations will not produce such a product. If solutions of sodium nitrate and ammonium chloride are mixed, no reaction occurs. One could write a molecular equation showing a double-replacement reaction, but both products, sodium chloride and ammonium nitrate, are soluble and would remain in the solution as ions. Every ion is a spectator ion and there is no net ionic equation at all. It is useful to be able to predict when a precipitate will occur in a reaction. To do so, you can use a set of guidelines called the **solubility rules** (Tables **6.2.1** and **6.2.2**).

Table **6.2.1**: Solubility Rules for Soluble Substances

| Soluble in Water | Important Exceptions (Insoluble) |
|---|---|
| All Group IA and $NH_4^+$ salts | none |
| All nitrates, chlorates, perchlorates and acetates | none |
| All sulfates | $CaSO_4$, $BaSO_4$, $SrSO_4$, $PbSO_4$ |
| All chlorides, bromides, and iodides | AgX, $Hg_2X_2$, $PbX_2$ (X= Cl, Br, or I) |

Table **6.2.2**: Solubility Rules for Sparingly Soluble Substances

| Sparingly Soluble in Water | Important Exceptions (Soluble) |
|---|---|
| All carbonates and phosphates | Group IA and $NH_4^+$ salts |
| All hydroxides | Group IA and $NH_4^+$ salts; $Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$ sparingly soluble |
| All sulfides | Group IA, IIA and $NH_4^+$ salts; MgS, CaS, BaS sparingly soluble |
| All oxalates | Group IA and $NH_4^+$ salts |
| Special note: The following electrolytes are of only moderate solubility in water: $CH_3COOAg$, $Ag_2SO_4$, $KClO_4$. They will precipitate only if rather concentrated solutions are used. | |

As an example on how to use the solubility rules, predict if a precipitate will form when solutions of cesium bromide and lead (II) nitrate are mixed.

$$Cs^+(aq) + Br^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow ?$$

The potential precipitates from a double-replacement reaction are cesium nitrate and lead (II) bromide. According to the solubility rules table, cesium nitrate is soluble because all compounds containing the nitrate ion, as well as all compounds containing the alkali metal ions, are soluble. Most compounds containing the bromide ion are soluble, but lead (II) is an exception. Therefore, the cesium and nitrate ions are spectator ions and the lead (II) bromide is a precipitate. The balanced net ionic reaction is:

$$Pb^{2+}(aq) + 2Br^-(aq) \rightarrow PbBr_2(s)$$

### Example 6.2.1: Solubility

Classify each compound as soluble or insoluble

a. $Zn(NO3)2$
b. $PbBr2$
c. $Sr3(PO4)2$

**Solution**

a. All nitrates are soluble in water, so $Zn(NO3)2$ is soluble.

b. All bromides are soluble in water, except those combined with $Pb^{2+}$, so $PbBr_2$ is insoluble.
c. All phosphates are insoluble, so $Sr_3(PO_4)_2$ is insoluble.

### ? Exercise 6.2.1: Solubility

Classify each compound as soluble or insoluble.

a. $Mg(OH)_2$
b. KBr
c. $Pb(NO_3)_2$

**Answer a**

insoluble

**Answer b**

soluble

**Answer c**

soluble

## Summary

Substances that dissolve in water to yield ions are called electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water. Solubility rules allow prediction of what products will be insoluble in water.

## Contributions & Attributions


- 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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# 6.3: Precipitation Reactions

**Learning Objectives**

- To identify a precipitation reaction.
- Predict the product of a reaction involving two aqueous ionic compounds.

## Precipitation Reactions

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. When a colorless solution of silver nitrate is mixed with a yellow-orange solution of potassium dichromate, a reddish precipitate of silver dichromate is produced.

$$\mathrm{AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + KNO_3\,(aq)} \tag{6.3.1}$$

This unbalanced equation has the general form of an exchange reaction:

$$\mathrm{AC + BD \rightarrow \underset{insoluble}{AD} + BC} \tag{6.3.2}$$

Thus precipitation reactions are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called **double-displacement reactions**. Precipitation reactions are used to isolate metals that have been extracted from their ores, and to recover precious metals for recycling.



Video: Mixing potassium dichromate and silver nitrate together to initiate a precipitation reaction (Equation 6.3.1).

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 aqueous $\mathit{NaCl}$ solution is mixed with 500 mL of aqueous $\mathit{KBr}$ solution, the final solution has a volume of 1.00 L and contains $\mathrm{Na^+\,(aq)}$, $\mathrm{Cl^-\,(aq)}$, $\mathrm{K^+\,(aq)}$, and $\mathrm{Br^-\,(aq)}$. As you will see in (Figure 6.3.1), 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.

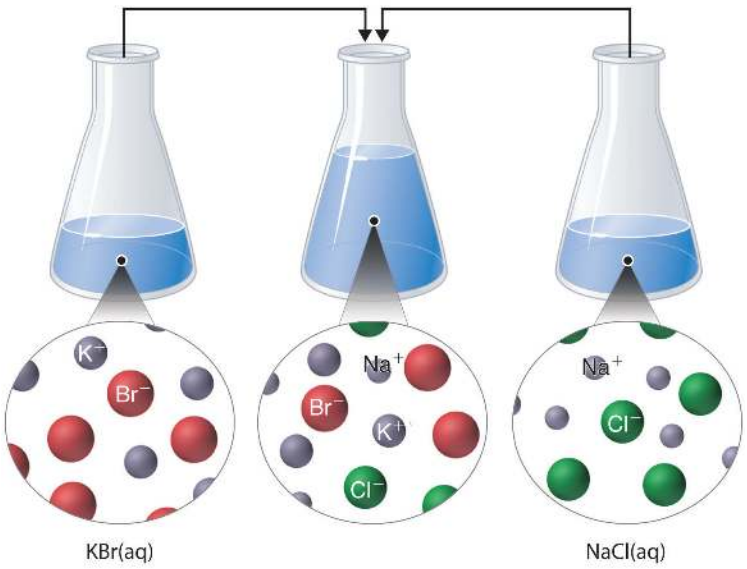


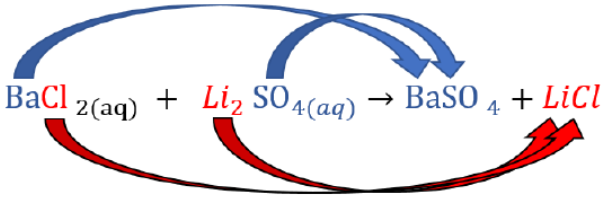

Figure **6.3.1**: The Effect of Mixing Aqueous **KBr** and **NaCl** Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

## Predicting Precipitation Reactions

A precipitation reaction occurs when a solid precipitate forms after mixing two strong electrolyte solutions. As stated previously, if none of the species in the solution reacts then no net reaction occurred.

Predict what will happen when aqueous solutions of barium chloride and lithium sulfate are mixed.

**Change the partners of the anions and cations on the reactant side to form new compounds (products):**




Chemical equation of the reactants barium chloride and lithium sulfate forming the products barium sulfate and lithium chloride.

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 **$BaSO_4$**.

### Correct the formulas of the products based on the charges of the ions.

No need to correct the formula as both compounds already have their charges balanced.

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4 + LiCl$$

### Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + LiCl\,(aq)$$

Table 7.5.1 from the previous section shows that **LiCl** is soluble in water, but **$BaSO_4$** is not soluble in water.

### Balance the equation:

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2\,LiCl\,(aq)$$

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.



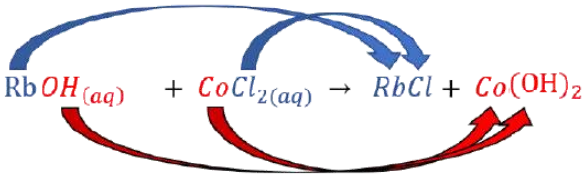
Figure **6.3.2**: An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.” A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. (Public Domain; Glitzy queen00 via Wikipedia).

## Example 6.3.1

Predict what will happen if aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.

### Solution

Solutions to Example 7.6.1

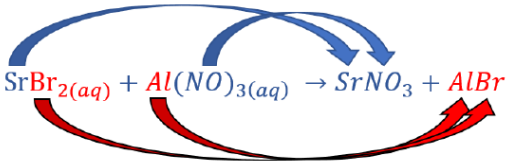
| Steps | Example |
|---|---|
| Change the partners of the anions and cations on the reactant side to form new compounds (products). |  Chemical equation of the reactants rubidium hydroxide and cobalt(II) chloride forming the products rubidium chloride and cobalt hydroxide. |
| Correct the formulas of the products based on the charges of the ions. | $\mathbf{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl + Co(OH)_2}$ |
| Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate. | $\mathbf{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl\,(aq) + Co(OH)_2\,(s)}$ |
| Balance the equation. | Coefficients already balanced. $\mathbf{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl\,(aq) + Co(OH)_2\,(s)}$ |

## Example 6.3.2

Predict what will happen if aqueous solutions of strontium bromide and aluminum nitrate are mixed.

### Solution

Solutions for Example 7.6.2

| Steps | Example |
|---|---|
| Change the partners of the anions and cations on the reactant side to form new compounds (products). |  Chemical equation of the reactants strontium bromide and aluminum nitrate forming the products strontium nitrate and aluminum bromide. |
| Correct the formulas of the products based on the charges of the ions. | $\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow Sr(NO_3)_2 + AlBr_3}$ |
| Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate. | $\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow Sr(NO_3)_2\,(aq) + AlBr_3\,(aq)}$ According to Table 7.5.1 from the previous section, both $\mathbf{AlBr_3}$ (rule 4) and $\mathbf{Sr(NO_3)_2}$ (rule 2) are soluble. |
| If all possible products are soluble, then no net reaction will occur. | $\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow}$ **NO REACTION** |

## ? Exercise 6.3.2

Using the information in Table 7.5.1 from the previous section, predict what will happen in each case involving strong electrolytes.

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**

$Fe(OH)_2$ precipitate is formed.

**Answer b**

$Hg_3(PO_4)_2$ precipitate is formed.

**Answer c**

No Reaction.

**Answer d**

$CaCO_3$ is precipitate formed.

## Summary

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when two electrolyte solutions are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

## Contributions & Attributions

- Modified by Joshua Halpern (Howard University)

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# 6.4: Oxidation–Reduction Reactions

**Learning Objectives**

- Define *oxidation, reduction, oxidizing agents, and reducing agents.*
- Recognize a reaction as an oxidation-reduction reaction.
- Identify the elements reduced or oxidized in a redox reaction.
- Identify oxidizing and reducing agents.

## Oxidation-Reduction - Transfer of Electrons

In the course of a chemical reaction between a metal and a nonmetal, electrons are transferred from the metal atoms to the nonmetal atoms. For example, when zinc metal is mixed with sulfur and heated, the compound zinc sulfide is produced. Two valence electrons from each zinc atom are transferred to each sulfur atom.

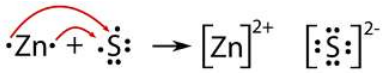


Figure **6.4.1**: Reaction between zinc and sulfur.

Since the zinc is losing electrons in the reaction, it is being oxidized. The sulfur is gaining electrons and is thus being reduced. An **oxidation-reduction reaction** is a reaction that involves the full or partial transfer of electrons from one reactant to another. **Oxidation** is the full or partial loss of electrons or the gain of oxygen. **Reduction** is the full or partial gain of electrons or the loss of oxygen. A **redox reaction** is another term for an oxidation-reduction reaction.

**Definition: Oxidation and Reduction**

An element is oxidized when it loses electrons.

An element is reduced when it gains electrons.

Each of these processes can be shown in a separate equation called a half-reaction. A **half-reaction** is an equation that shows either the oxidation or the reduction reaction that occurs during a redox reaction.

$$\underbrace{Zn \longrightarrow Zn_2^{2+} + e^-}_{\text{Oxidation}} \tag{6.4.1}$$

$$\underbrace{S^+ \; 2\,e^- \longrightarrow S^{2-}}_{\text{Reduction}} \tag{6.4.2}$$

It is important to remember that the two half-reactions occur simultaneously. The resulting ions that are formed are then attracted to one another in an ionic bond.

Another example of an oxidation-reduction reaction involving electron transfer is the well-known combination of metallic sodium and chlorine gas to form sodium chloride:

$$2\,Na^+Cl_2 \longrightarrow 2\,NaCl \tag{6.4.3}$$

The half-reactions are as follows:

$$\underbrace{2\,Na \longrightarrow 2\,Na^+ + 2\,e^-}_{\text{Oxidation}} \tag{6.4.4}$$

$$\underbrace{Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-}_{\text{Reduction}} \tag{6.4.5}$$

### Example 6.4.1: Formation of Sodium Bromide

Identify what is being oxidized and reduced in the following redox reaction.

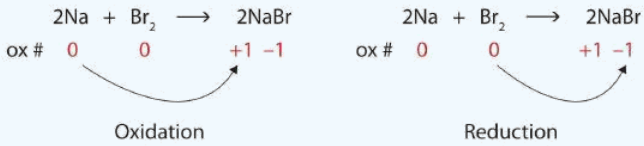
$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$

#### Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have a charge of 0. In the ionic product, the $Na^+$ ions have a charge of +1, while the $Br^-$ ions have a cahrge of −1.

$$\overset{0}{2Na} + \overset{0}{Br_2} \rightarrow \overset{+1-1}{2NaBr}$$

Sodium is increasing its charge from 0 to +1, so it is being oxidized; bromine is decreasing its charge from 0 to −1, so it is being reduced:




Equation of sodium and bromine reacting, labeled with sodium's oxidation number change from 0 to +1 and bromine's oxidation number change from 0 to -1

Because charges are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

We often talk about species that cause something to be oxidized or reduced because we may need to create a specific change in a compound. For example, a common way to remove stains in clothing is to oxidize the stain, which requires a compound that causes oxidation. A compound that causes oxidation is an **oxidizing agent**. Conversely, a **reducing agent** is a compound that causes reduction.

## Oxidation-Reduction with Oxygen and Hydrogen

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of **oxidation** was "**adding oxygen**," so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for **reduction**: if a molecule **loses oxygen** atoms, the molecule is being reduced. For example, the acetaldehyde ($CH_3CHO$) molecule takes on an oxygen atom to become acetic acid ($CH_3COOH$).

$$2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH$$

Thus, acetaldehyde is being oxidized.

Similarly, **reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms**. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol ($CH_3CH_2OH$), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

| Process | Change in oxygen (some reactions) | Change in hydrogen (some reactions) |
|---|---|---|
| Oxidation | gain | lose |
| Reduction | lose | gain |

### Example 6.4.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $N_2 \rightarrow NH_3$

b. $CH_3CH_2OHCH_3 \rightarrow CH_3COCH_3$
c. $HCHO \rightarrow HCOOH$

**Solution**

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

**? Exercise 6.4.2**

In each conversion, indicate whether oxidation or reduction is occurring.

a. $CH_4 \rightarrow CO_2 + H_2O$
b. $NO_2 \rightarrow N_2$
c. $CH_2{=}CH_2 \rightarrow CH_3CH_3$

**Answer a:**

Oxygen is being added. Oxidation is occurring.

**Answer b:**

Oxygen is being removed. Reduction is occurring.

**Answer a:**

Hydrogen is being added. Reduction is occurring.

## Key Takeaway

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

# Contributors & Affiliations

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# 6.5: Acids, Bases, and Neutralization Reactions

**Learning Objectives**

- Identify an acid-base neutralization reaction and predict its products.

Acids and Bases are common compounds we encounter in nature and the world around us. We will spend time in later sections looking at acid-base properties, but here, we want to think about them as a type of chemical reaction.

## Acids and Bases

An **acid** is any compound that produces hydrogen ions ($H^+$) in an aqueous solution, and the chemical opposite of an acid is a **base**, which is a compound that produces hydroxide ions ($OH^-$) in an aqueous solution. These original definitions were proposed by Arrhenius (the same person who proposed ion dissociation) in 1884, so they are referred to as the **Arrhenius definition** of an acid and a base, respectively.

You may recognize that, based on the description of a hydrogen atom, an $H^+$ ion is a hydrogen atom that has lost its lone electron; that is, $H^+$ is simply a proton. Do we really have bare protons moving about in aqueous solution? No. What is more likely is that the $H^+$ ion has attached itself to one (or more) water molecule(s). To represent this chemically, we define the **hydronium ion** as $H_3O^+$, which represents an additional proton attached to a water molecule. We use the hydronium ion as the more logical way that a hydrogen ion appears in an aqueous solution, although in many chemical reactions $H^+$ and $H_3O^+$ are treated equivalently.

## Acid-Base Neutralization Reactions

The reaction of an acid and a base is called a **neutralization reaction**. Although acids and bases have their own unique chemistries, the acid and base "cancel" each other's chemistry to produce a rather innocuous substance—water. In fact, the general reaction between an acid and a base is:

$$\text{acid} + \text{base} \longrightarrow \text{water} + \text{salt}$$

where the term **salt** is generally used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base. (In chemistry, the word *salt* refers to more than just table salt.) For example, the balanced chemical equation for the reaction between HCl(aq) and KOH(aq) is

$$\mathrm{HCl(aq) + KOH(aq) \longrightarrow H_2O(\ell) + KCl(aq)}$$

where the salt is KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the reaction between HCl(aq) and $Mg(OH)_2$(aq), additional molecules of HCl and $H_2O$ are required to balance the chemical equation:

$$\mathrm{2\,HCl(aq) + Mg(OH)_2(aq) \longrightarrow 2\,H_2O(\ell) + MgCl_2(aq)}$$

Here, the salt is $MgCl_2$. (This is one of several reactions that take place when a type of antacid—a base—is used to treat stomach acid.)

**6.5.1 Example :**

Write the neutralization reactions between each acid and base.

a. $HNO_3$(aq) and $Ba(OH)_2$(aq)
b. $H_3PO_4$(aq) and $Ca(OH)_2$(aq)

**Solution**

First, we will write the chemical equation with the formulas of the reactants and the expected products; then we will balance the equation.

a. The expected products are water and barium nitrate, so the initial chemical reaction is

$$\mathrm{HNO_3(aq) + Ba(OH)_2(aq) \longrightarrow H_2O(\ell) + Ba(NO_3)_2(aq)}$$

To balance the equation, we need to realize that there will be two $H_2O$ molecules, so two $HNO_3$ molecules are required:

$$2\,HNO_3(aq) + Ba(OH)_2(aq) \longrightarrow 2\,H_2O(\ell) + Ba(NO_3)_2(aq)$$

This chemical equation is now balanced.

b. The expected products are water and calcium phosphate, so the initial chemical equation is

$$H_3PO_4(aq) + Ca(OH)_2(aq) \longrightarrow H_2O(\ell) + Ca_3(PO_4)_2(s)$$

According to the solubility rules, $Ca_3(PO_4)_2$ is insoluble, so it has an (s) phase label. To balance this equation, we need two phosphate ions and three calcium ions. We end up with six water molecules to balance the equation:

$$2\,H_3PO_4(aq) + 3\,Ca(OH)_2(aq) \longrightarrow 6\,H_2O(\ell) + Ca_3(PO_4)_2(s)$$

This chemical equation is now balanced.

### 6.5.1 Exercise

Write the neutralization reaction between $H_2SO_4(aq)$ and $Sr(OH)_2(aq)$.

**Answer**

$$H_2SO_4(aq) + Sr(OH)_2(aq) \longrightarrow 2\,H_2O(\ell) + SrSO_4(aq)$$

Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between HCl(aq) and $Fe(OH)_3(s)$ still proceeds according to the equation:

$$3\,HCl(aq) + Fe(OH)_3(s) \longrightarrow 3\,H_2O(\ell) + FeCl_3(aq)$$

even though $Fe(OH)_3$ is not soluble. When one realizes that $Fe(OH)_3(s)$ is a component of rust, this explains why some cleaning solutions for rust stains contain acids—the neutralization reaction produces products that are soluble and wash away. (Washing with acids like HCl is one way to remove rust and rust stains, but HCl must be used with caution!)

## Key Takeaways

- The Arrhenius definition of an acid is a substance that increases the amount of $H^+$ in an aqueous solution.
- The Arrhenius definition of a base is a substance that increases the amount of $OH^-$ in an aqueous solution.
- Neutralization is the reaction of an acid and a base, which forms water and a salt.

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# CHAPTER OVERVIEW

## 7: Gases


7.1: Kinetic Molecular Theory- A Model for Gases
7.2: Pressure - The Result of Constant Molecular Collisions
7.3: Boyle’s Law - Pressure and Volume
7.4: Charles’s Law- Volume and Temperature
7.5: Gay-Lussac's Law- Temperature and Pressure
7.6: Avogadro’s Law- Volume and Moles
7.7: The Ideal Gas Law- Pressure, Volume, Temperature, and Moles
7.8: Mixtures of Gases - Why Deep-Sea Divers Breathe a Mixture of Helium and Oxygen


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# 7.1: Kinetic Molecular Theory- A Model for Gases

**Learning Objectives**

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**.

## Kinetic Theory of Gases

The kinetic theory of gases is based on the following statements (*often referred to as the ideal gas assumptions*):

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic; that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure 7.1.1 shows a representation of how we mentally picture the gas phase.

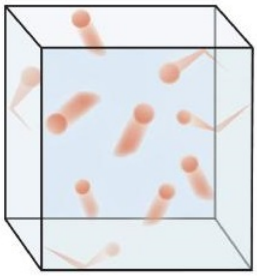


Figure 7.1.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

This model of gases explains some of the physical properties of gases. Because most of a gas is empty space, a gas has a low density and can expand or contract under the appropriate influence. The fact that gas particles are in constant motion means that two or more gases will always mix, as the particles from the individual gases move and collide with each other.

An **ideal gas** is a gas that exactly follows the statements of the kinetic theory. Unfortunately, *real gases* are not ideal. Many gases deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements so well that the kinetic theory of gases is well accepted by the scientific community.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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# 7.2: Pressure - The Result of Constant Molecular Collisions

**Learning Objectives**

- Define *pressure*.
- Learn the units of pressure and how to convert between them.

## Pressure

The kinetic theory of gases indicates that gas particles are always in motion and are colliding with other particles and the walls of the container holding them. Although collisions with container walls are elastic (i.e., there is no net energy gain or loss because of the collision), a gas particle does exert a force on the wall during the collision. The accumulation of all these forces distributed over the area of the walls of the container causes something we call pressure. **Pressure** (***P***) is defined as the force of all the gas particle/wall collisions divided by the area of the wall:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

All gases exert pressure; it is one of the fundamental measurable quantities of this phase of matter. Even our atmosphere exerts pressure—in this case, the gas is being "held in" by the earth's gravity, rather than the gas being in a container. The pressure of the atmosphere is about 14.7 pounds of force for every square inch of surface area: 14.7 $\text{lb/in}^2$.

## Pressure Units

Pressure has a variety of units. The formal, SI-approved unit of pressure is the *pascal* (Pa), which is defined as 1 $\text{N/m}^2$ (one newton of force over an area of one square meter). However, this is usually too small in magnitude to be useful. A common unit of pressure is the **atmosphere** (atm), which was originally defined as the average atmospheric pressure at sea level.

However, "average atmospheric pressure at sea level" is difficult to pinpoint because of atmospheric pressure variations. A more reliable and common unit is **millimeters of mercury** (mmHg), which is the amount of pressure exerted by a column of mercury exactly 1 mm high. An equivalent unit is the **torr**, which equals 1 mmHg. (The torr is named after Evangelista Torricelli, a seventeenth-century Italian scientist who invented the mercury barometer.) With these definitions of pressure, the atmosphere unit is redefined: 1 atm is defined as exactly 760 mmHg, or 760 torr. We thus have the following equivalents:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr}$$

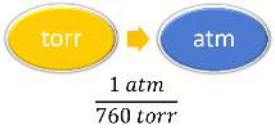
We can use these equivalents as with any equivalence—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

**Example 7.2.1: Pressure Conversion**

How many atmospheres are there in 595 torr?

**Solution**

Solutions to Example 11.3.1

| Steps for Problem Solving | Unit Conversion |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: 595 torr<br>Find: ? atm |
| List other known quantities. | 1 atm = 760 torr |
| Prepare a concept map. |  |
| Cancel units and calculate. | $595\ \cancel{torr} \times \frac{1\ atm}{760\ \cancel{torr}} = 0.783\ atm$ |
| Think about your result. | 595 torr is less than 760 torr so the final answer should be less than 1 atm. |

## Exercise 7.2.1

How many atmospheres are there in 1,022 torr?

**Answer**

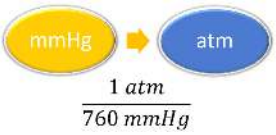
1.345 atm

## Example 7.2.2: Mars

The atmosphere on Mars is largely $CO_2$ at a pressure of 6.01 mmHg. What is this pressure in atmospheres?

### Solution

Solutions to Example 11.3.2

| Steps for Problem Solving | Unit Conversion |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: 6.01mmHg<br>Find: ? atm |
| List other known quantities. | 1 atm = 760 mmHg |
| Prepare a concept map. |  |
| Cancel units and calculate. | $6.01\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$ |
| Think about your result. | 6.01 is a very small number relative to 760 mmHg, just like the value in atmospheres. |

## Exercise 7.2.2

Atmospheric pressure is low in the eye of a hurricane. In a 1979 hurricane in the Pacific Ocean, a pressure of 0.859 atm was reported inside the eye. What is this pressure in torr?

**Answer**

652 torr

## Summary

- Pressure is a force exerted over an area.
- Pressure has several common units that can be converted.

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# 7.3: Boyle's Law - Pressure and Volume

**Learning Objectives**

- Learn what is meant by the term *gas laws*.
- Learn and apply Boyle's Law.
- Calculate changes in a gas' pressure and volume at constant temperature and moles.

## Boyle's Law

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure ($P$) and volume ($V$), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [$n$]), if the temperature ($T$) of the gas was kept constant, pressure and volume were related: as one increases, the other decreases. As one decreases, the other increases. This means that pressure and volume are *inversely related*.

There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant for a given amount of gas at a constant temperature:

$$P \times V = \text{ constant at constant n and T}$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled $P_1$ and $V_1$ and the new conditions are labeled $P_2$ and $V_2$, we have

$$P_1V_1 = \text{constant} = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \text{ at constant n and T}$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called **Boyle's Law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure **7.3.1** shows two representations of how Boyle's Law works.

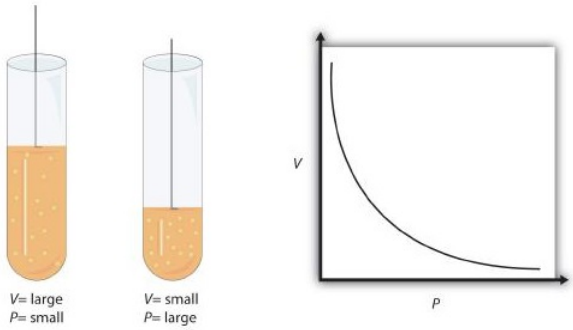



Figure **7.3.1**: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot $P$ versus $V$ for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Boyle's Law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in

Boyle's Law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won't matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

### Example 7.3.1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

**Solution**

Solutions to Example 11.8.1

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: $P_1$ = 2.44 atm and $V_1$ = 4.01 L<br>$P_2$ = 1.93 atm<br>Find: $V_2$ = ? L |
| List other known quantities. | none |
| Plan the problem. | First, rearrange the equation algebraically to solve for $V_2$.<br>$$V_2 = \frac{P_1 \times V_1}{P_2}$$ |
| Cancel units and calculate. | Now substitute the known quantities into the equation and solve.<br>$$V_2 = \frac{2.44 \cancel{\text{ atm}} \times 4.01 \text{ L}}{1.93 \cancel{\text{ atm}}} = 5.07 \text{ L}$$ |
| Think about your result. | We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's Law. |

### Exercise 7.3.1

If $P_1$ = 334 torr, $V_1$ = 37.8 mL, and $P_2$ = 102 torr, what is $V_2$?

**Answer**

124 mL

As mentioned, you can use any units for pressure and volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

### Example 7.3.2:

A sample of gas has an initial pressure of 722 torr and an initial volume of 88.8 mL. Its volume changes to 0.663 L. What is the new pressure?

**Solution**

Solutions to Example 11.8.2

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: $P_1$ = 722 torr and $V_1$ = 88.8 mL<br>$V_2$ = 0.633 L<br>Find: $P_2$ = ? torr |
| List other known quantities. | 1 L = 1000 mL to have the same units for volume. |
| Plan the problem. | 1. Perform the conversion of the second volume unit from L to mL.<br>2. Rearrange the equation algebraically to solve for $P_2$.<br>$$P_2 = \frac{P_1 \times V_1}{V_2}$$ |
| Cancel units and calculate. | 1.<br>$$0.663 \cancel{L} \times \frac{1000\,ml}{1\,\cancel{L}} = 663\,ml$$<br>2. Substitute the known quantities into the equation and solve.<br>$$P_2 = \frac{722\ \text{torr} \times 88.8\ \cancel{mL}}{663\ \cancel{mL}} = 96.7\ \text{torr}$$ |
| Think about your result. | When the volume increased, the pressure decreased, which is as expected for Boyle's Law. |

**? Exercise 7.3.2**

If $V_1$ = 456 mL, $P_1$ = 308 torr, and $P_2$ = 1.55 atm, what is $V_2$?

**Answer**

119 mL

## Summary

- The behavior of gases can be modeled with gas laws.
- Boyle's Law relates the pressure and volume of a gas at constant temperature and amount.

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# 7.4: Charles's Law- Volume and Temperature

**Learning Objectives**

- Learn and apply Charles's Law.
- Calculate changes in a gas' volume and temperature at constant pressure and moles.

Everybody enjoys the smell and taste of freshly-baked bread. It is light and fluffy as a result of the action of yeast on sugar. The yeast converts the sugar to carbon dioxide, which at high temperatures causes the dough to expand. The end result is an enjoyable treat, especially when covered with melted butter.

## Charles's Law

French physicist Jacques Charles (1746-1823) studied the effect of temperature on the volume of a gas at constant pressure. **Charles's Law** states that the volume of a given mass of gas varies directly with the absolute temperature of the gas when pressure is kept constant. The absolute temperature is temperature measured with the Kelvin scale. The Kelvin scale must be used because zero on the Kelvin scale corresponds to a complete stop of molecular motion.

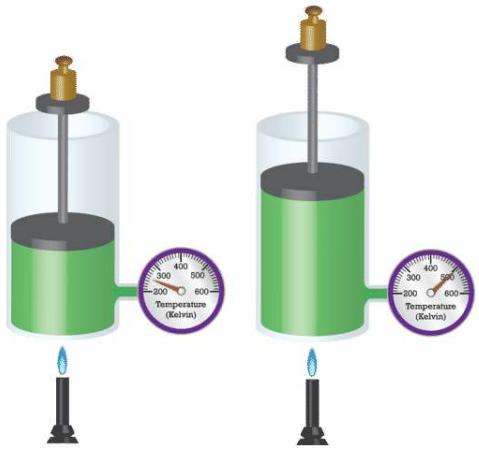



Figure **7.4.1**: As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

Mathematically, the direct relationship of Charles's Law can be represented by the following equation:

$$\frac{V}{T} = k$$

As with Boyle's Law, $k$ is constant only for a given gas sample. The table below shows temperature and volume data for a set amount of gas at a constant pressure. The third column is the constant for this particular data set and is always equal to the volume divided by the Kelvin temperature.

Table **7.4.1**: Temperature-Volume Data

| Temperature (K) | Volume (mL) | $\frac{V}{T} = k \left(\frac{\text{mL}}{\text{K}}\right)$ |
|---|---|---|
| 50 | 20 | 0.40 |
| 100 | 40 | 0.40 |
| 150 | 60 | 0.40 |
| 200 | 80 | 0.40 |
| 300 | 120 | 0.40 |
| 500 | 200 | 0.40 |
| 1000 | 400 | 0.40 |

When this data is graphed, the result is a straight line, indicative of a direct relationship, shown in the figure below.

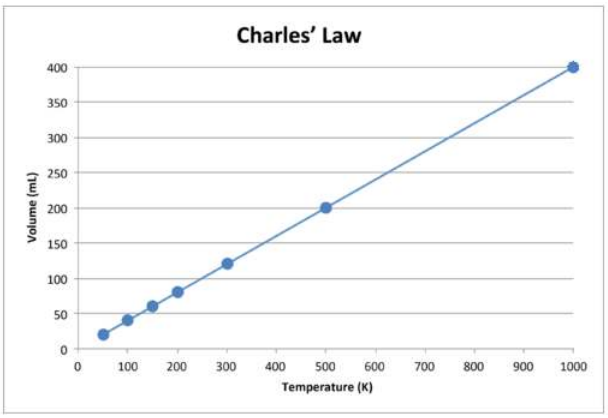



Figure 7.4.2:The volume of a gas increases as the Kelvin temperature increases.

Notice that the line goes exactly toward the origin, meaning that as the absolute temperature of the gas approaches zero, its volume approaches zero. However, when a gas is brought to extremely cold temperatures, its molecules would eventually condense into the liquid state before reaching absolute zero. The temperature at which this change into the liquid state occurs varies for different gases.

Charles's Law can also be used to compare changing conditions for a gas. Now we use $V_1$ and $T_1$ to stand for the initial volume and temperature of a gas, while $V_2$ and $T_2$ stand for the final volume and temperature. The mathematical relationship of Charles's Law becomes:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This equation can be used to calculate any one of the four quantities if the other three are known. The direct relationship will only hold if the temperatures are expressed in Kelvin. Temperatures in Celsius will not work. Recall the relationship that $\text{K} = {}^\circ\text{C} + 273$.

**Example 7.4.1:**

A balloon is filled to a volume of $2.20\ \text{L}$ at a temperature of $22^\circ\text{C}$. The balloon is then heated to a temperature of $71^\circ\text{C}$. Find the new volume of the balloon.

**Solution**

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>$V_1 = 2.20\ \text{L}$ and<br>$T_1 = 22°\text{C} = 295\ \text{K}$<br>$T_2 = 71°\text{C} = 344\ \text{K}$<br>Find: $V_2$ = ? L |
| List other known quantities. | The temperatures have first been converted to Kelvin. |
| Plan the problem. | First, rearrange the equation algebraically to solve for $V_2$.<br>$$V_2 = \frac{V_1 \times T_2}{T_1}$$ |
| Cancel units and calculate. | Now substitute the known quantities into the equation and solve.<br>$$V_2 = \frac{2.20\ \text{L} \times 344\ \cancel{\text{K}}}{295\ \cancel{\text{K}}} = 2.57\ \text{L}$$ |
| Think about your result. | The volume increases as the temperature increases. The result has three significant figures. |

**? Exercise 7.4.1**

If $V_1$ = 3.77 L and $T_1$ = 255 K, what is $V_2$ if $T_2$ = 123 K?

**Answer**

1.82 L

**✔ Example 7.4.2:**

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must be the temperature of the gas for its volume to be 25.0 L?

**Solution**

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>Given:$T_1$ = -27°C and $V_1$ = 34.8 L<br>$V_2$ = 25.0 L<br>Find: $T_2$ = ? K |
| List other known quantities. | K = -27°C + 273 |
| Plan the problem. | 1. Convert the initial temperature to Kelvin<br>2. Rearrange the equation algebraically to solve for $T_2$.<br>$$T_2 = \frac{V_2 \times T_1}{V_1}$$ |
| Cancel units and calculate. | 1. −67°C + 273 = 206 K<br>2. Substitute the known quantities into the equation and solve.<br>$$T_2 = \frac{25.0 \cancel{L} \times 206\ \text{K}}{34.8 \cancel{L}} = 148\ \text{K}$$ |
| Think about your result. | This is also equal to −125°C. As temperature decreases, volume decreases—which it does in this example. |

**? Exercise 7.4.2**

If $V_1$ = 623 mL, $T_1$ = 255°C, and $V_2$ = 277 mL, what is $T_2$?

**Answer**

235 K, or −38°C

## Summary

- Charles's Law relates the volume and temperature of a gas at constant pressure and amount.

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# 7.5: Gay-Lussac's Law- Temperature and Pressure

**Learning Objectives**

- Explain Gay-Lussac's Law.
- Calculate changes in a gas' pressure and temperature at constant volume and moles.

Propane tanks are widely used with barbeque grills. But it's not fun to find out halfway through grilling that you have run out of gas. You can buy gauges that measure the pressure inside the tank to see how much is left. The gauge measures pressure and will register a higher pressure on a hot day than it will on a cold day. So you need to take the air temperature into account when you decide whether or not to refill the tank before your next cook-out.

## Gay-Lussac's Law

When the temperature of a sample of gas in a rigid container is increased, the pressure of the gas increases as well. The increase in kinetic energy results in the molecules of gas striking the walls of the container with more force, resulting in a greater pressure. The French chemist Joseph Gay-Lussac (1778-1850) discovered the relationship between the pressure of a gas and its absolute temperature. **Gay-Lussac's Law** states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant. Gay-Lussac's Law is very similar to Charles's Law, with the only difference being the type of container. Whereas the container in a Charles's Law experiment is flexible, it is rigid in a Gay-Lussac's Law experiment.



Figure **7.5.1**: Joseph Gay-Lussac.

The mathematical expressions for Gay-Lussac's Law are likewise similar to those of Charles's Law:

$$\frac{P}{T} \text{ and } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

A graph of pressure vs. temperature also illustrates a direct relationship. As a gas is cooled at constant volume, its pressure continually decreases until the gas condenses to a liquid.

**Example 7.5.1**

The gas in an aerosol can is under a pressure of $3.00\ \text{atm}$ at a temperature of $25°C$. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of $845°C$?

**Solution**

Solutions to Example 11.10.1

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>$P_1 = 3.00\ \text{atm}$<br>$T_1 = 25°\text{C} = 298\ \text{K}$<br>$T_2 = 845°\text{C} = 1118\ \text{K}$<br>Find: $P_2 = ?\ \text{atm}$ |
| List other known quantities. | The temperatures have first been converted to Kelvin. |
| Plan the problem. | First, rearrange the equation algebraically to solve for $P_2$.<br>$$P_2 = \frac{P_1 \times T_2}{T_1}$$ |
| Calculate. | Now substitute the known quantities into the equation and solve.<br>$$P_2 = \frac{3.00\ \text{atm} \times 1118\ \cancel{\text{K}}}{298\ \cancel{\text{K}}} = 11.3\ \text{atm}$$ |
| Think about your result. | The pressure increases dramatically due to a large increase in temperature. |

## Summary

- Pressure and temperature at constant volume are directly proportional.

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# 7.6: Avogadro's Law- Volume and Moles

**Learning Objectives**

- Explain Avogadro's Law.
- Calculate changes in a gas' volume and moles at constant pressure and temperature.

A flat tire is not very useful. It does not cushion the rim of the wheel and creates a very uncomfortable ride. When air is added to the tire, the pressure increases as more molecules of gas are forced into the rigid tire. How much air should be put into a tire depends on the pressure rating for that tire. Too little pressure and the tire will not hold its shape. Too much pressure and the tire could burst.

## Avogadro's Law

You have learned about Avogadro's hypothesis: equal volumes of any gas at the same temperature and pressure contain the same number of molecules. It follows that the volume of a gas is directly proportional to the number of moles of gas present in the sample. **Avogadro's Law** states that the volume of a gas is directly proportional to the number of moles (or number of particles) of gas when the temperature and pressure are held constant. The mathematical expression of Avogadro's Law is:

$$V = k \times n$$

or

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

where $n$ is the number of moles of gas and $k$ is a constant. Avogadro's Law is in evidence whenever you blow up a balloon. The volume of the balloon increases as you add moles of gas to the balloon by blowing it up.

If the container holding the gas is rigid rather than flexible, pressure can be substituted for volume in Avogadro's Law. Adding gas to a rigid container makes the pressure increase.

**Example 7.6.1**

A balloon has been filled to a volume of $1.90\ \text{L}$ with $0.0920\ \text{mol}$ of helium gas. If $0.0210\ \text{mol}$ of additional helium is added to the balloon while the temperature and pressure are held constant, what is the new volume of the balloon?

**Solution**

Solutions to Example 11.11.1

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>$V_1 = 1.90\ \text{L}$<br>$n_1 = 0.0920\ \text{mol}$<br>Find: $V_2 = ?\ \text{L}$ |
| List other known quantities. | Note that the final number of moles has to be calculated by adding the original number of moles to the moles of added helium.<br>$n_2 = 0.0920 + 0.0210 = 0.1130\ \text{mol}$ |
| Plan the problem. | First, rearrange the equation algebraically to solve for $V_2$.<br>$$V_2 = \frac{V_1 \times n_2}{n_1}$$ |
| Calculate. | Now substitute the known quantities into the equation and solve.<br>$$V_2 = \frac{1.90\ \text{L} \times 0.1130\ \cancel{\text{mol}}}{0.0920\ \cancel{\text{mol}}} = 2.33\ \text{L}$$ |
| Think about your result. | Since a relatively small amount of additional helium was added to the balloon, its volume increases slightly. |

**? Exercise 7.6.1**

A 12.8 L volume of gas contains .000498 moles of oxygen gas. At constant temperature and pressure, what volume does .0000136 moles of the gas fill?

**Answer**

0.350 L

## Summary

- Calculations for relationships between volume and number of moles of a gas can be performed using Avogadro's Law.

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# 7.7: The Ideal Gas Law- Pressure, Volume, Temperature, and Moles

**Learning Objectives**

- Explain the Ideal Gas Law.
- Use the ideal gas law to calculate the pressure, volume, temperature, or moles of a gas.

There are a number of chemical reactions that require ammonia. In order to carry out the reaction efficiently, we need to know how much ammonia we have for stoichiometric purposes. Using gas laws, we can determine the number of moles present in the tank if we know the volume, temperature, and pressure of the system.

## Ideal Gas Law

The Combined Gas Law shows that the pressure of a gas is inversely proportional to volume and directly proportional to temperature. Avogadro's Law shows that volume or pressure is directly proportional to the number of moles of gas. Putting these together leaves us with the following equation:

$$\frac{P_1 \times V_1}{T_1 \times n_1} = \frac{P_2 \times V_2}{T_2 \times n_2}$$

As with the other gas laws, we can also say that $\frac{(P \times V)}{(T \times n)}$ is equal to a constant. The constant can be evaluated provided that the gas being described is considered to be ideal.

The **Ideal Gas Law** is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas. If we substitute in the variable $R$ for the constant, the equation becomes:

$$\frac{P \times V}{T \times n} = R$$

The Ideal Gas Law is conveniently rearranged to look this way, with the multiplication signs omitted:

$$PV = nRT$$

The variable $R$ in the equation is called the **ideal gas constant**.

## Evaluating the Ideal Gas Constant

The value of $R$, the ideal gas constant, depends on the units chosen for pressure, temperature, and volume in the ideal gas equation. It is necessary to use Kelvin for the temperature and it is conventional to use the SI unit of liters for the volume. However, pressure is commonly measured in one of three units: $\mathbf{kPa}$, $\mathbf{atm}$, or $\mathbf{mm\ Hg}$. Therefore, $R$ can have three different values.

We will demonstrate how $R$ is calculated when the pressure is measured in $\mathbf{kPa}$. The volume of $\mathbf{1.00\ mol}$ of any gas at STP (Standard temperature, 273.15 K and pressure, 1 atm) is measured to be $\mathbf{22.414\ L}$. We can substitute $\mathbf{101.325\ kPa}$ for pressure, $\mathbf{22.414\ L}$ for volume, and $\mathbf{273.15\ K}$ for temperature into the ideal gas equation and solve for $R$.

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{101.325\ \text{kPa} \times 22.414\ \text{L}}{1.000\ \text{mol} \times 273.15\ \text{K}} \\ &= 8.314\ \text{kPa} \cdot \text{L/K} \cdot \text{mol} \end{aligned}$$

This is the value of $R$ that is to be used in the ideal gas equation when the pressure is given in $\mathbf{kPa}$. The table below shows a summary of this and the other possible values of $R$. It is important to choose the correct value of $R$ to use for a given problem.

Table **7.7.1**: Values of the Ideal Gas Constant

| Unit of $P$ | Unit of $V$ | Unit of $n$ | Unit of $T$ | Value and Unit of $R$ |
|---|---|---|---|---|
| kPa | L | mol | K | $8.314\ \text{J/K} \cdot \text{mol}$ |
| atm | L | mol | K | $0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol}$ |
| mm Hg | L | mol | K | $62.36\ \text{L} \cdot \text{mm Hg/K} \cdot \text{mol}$ |

Notice that the unit for $R$ when the pressure is in kPa has been changed to $\text{J/K} \cdot \text{mol}$. A kilopascal multiplied by a liter is equal to the SI unit for energy, a joule (J).

## Example 7.7.1 Oxygen Gas

What volume is occupied by 3.76 g of oxygen gas at a pressure of 88.4 kPa and a temperature of 19°C? Assume the oxygen is ideal.

### Solution

Solutions to Example 11.5.1

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>• $P = 88.4\ \text{kPa}$<br>• $T = 19°\text{C} = 292\ \text{K}$<br>Mass $\text{O}_2 = 3.76\ \text{g}$<br>Find: $V$ = ? L |
| List other known quantities. | $\text{O}_2 = 32.00\ \text{g/mol}$<br>$R = 8.314\ \text{J/K} \cdot \text{mol}$ |
| Plan the problem. | 1. First, determine the number of moles of $\text{O}_2$ from the given mass and the molar mass.<br>2. Then, rearrange the equation algebraically to solve for V<br>$$V = \frac{nRT}{P}$$ |
| Calculate. | 1.<br>$$3.76\ \cancel{g} \times \frac{1\ \text{mol O}_2}{32.00\ \cancel{g}\ \text{O}_2} = 0.1175\ \text{mol O}_2$$<br>2. Now substitute the known quantities into the equation and solve.<br>$$V = \frac{nRT}{P}$$<br>$$= \frac{0.1175\ \cancel{\text{mol}} \times 8.314\ \cancel{\text{J/K}} \cdot \cancel{\text{mol}} \times 292\ \cancel{\text{K}}}{88.4\ \cancel{\text{kPa}}}$$<br>$$= 3.23\ \text{L O}_2$$ |
| Think about your result. | The number of moles of oxygen is far less than one mole, so the volume should be fairly small compared to molar volume $(22.4\ \text{L/mol})$ since the pressure and temperature are reasonably close to standard. The result has three significant figures because of the values for $T$ and $P$. Since a joule $(\text{J}) = \text{kPa} \cdot \text{L}$, the units cancel out correctly, leaving a volume in liters. |

## Example 7.7.2: Argon Gas

A 4.22 mol sample of Ar has a pressure of 1.21 atm and a temperature of 34°C. What is its volume?

### Solution

Solutions to Example 11.5.2

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>n = 4.22 mol<br>P = 1.21 atm<br>T = 34°C<br>Find: $V$ = ? L |
| List other known quantities. | none |
| Plan the problem. | 1. The first step is to convert temperature to Kelvin.<br>2. Then, rearrange the equation algebraically to solve for V<br>$$V = \frac{nRT}{P}$$ |
| Calculate. | 1. 34 + 273 = 307 K<br>2. Now substitute the known quantities into the equation and solve.<br>$$V = \frac{(4.22\ \cancel{mol})(0.08205\frac{L.\cancel{atm}}{\cancel{mol.K}})(307\ \cancel{K})}{1.21\ \cancel{atm}}$$<br>$$= 87.9\ L$$ |
| Think about your result. | The number of moles of Ar is large so the expected volume should also be large. |

## Exercise 7.7.1

A 0.0997 mol sample of $O_2$ has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

**Answer**

3.94 L

## Exercise 7.7.2

For a 0.00554 mol sample of $H_2$, $P$ = 23.44 torr and $T$ = 557 K. What is its volume?

**Answer**

8.21 L

## Summary

- The Ideal Gas Law is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas.

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# 7.8: Mixtures of Gases - Why Deep-Sea Divers Breathe a Mixture of Helium and Oxygen

**Learning Objectives**

- Explain Dalton's Law of Partial Pressures.
- Calculate the total or partial pressure of a gas mixture.

The atmosphere of Venus is markedly different from that of Earth. The gases in the Venusian atmosphere are $96.5\%$ carbon dioxide and $3\%$ nitrogen. The atmospheric pressure on Venus is roughly 92 times that of Earth, so the amount of nitrogen on Venus would contribute a pressure well over $2700\ \text{mm Hg}$. And there is no oxygen present, so we couldn't breathe there. Not that we would want to go to Venus, as the surface temperature is usually over $460°\text{C}$.

## Dalton's Law of Partial Pressures

Gas pressure results from collisions between gas particles and the inside walls of their container. If more gas is added to a rigid container, the gas pressure increases. The identities of the two gases do not matter. John Dalton, the English chemist who proposed the atomic theory, also studied mixtures of gases. He found that each gas in a mixture exerts a pressure independently of every other gas in the mixture. For example, our atmosphere is composed of about $78\%$ nitrogen and $21\%$ oxygen, with smaller amounts of several other gases making up the rest. Since nitrogen makes up $78\%$ of the gas particles in a given sample of air, it exerts $78\%$ of the pressure. If the overall atmospheric pressure is $1.00\ \text{atm}$, then the pressure of just the nitrogen in the air is $0.78\ \text{atm}$. The pressure of the oxygen in the air is $0.21\ \text{atm}$.

The **partial pressure** of a gas is the contribution that gas makes to the total pressure when the gas is part of a mixture. The partial pressure of nitrogen is represented by $P_{N_2}$. **Dalton's Law of Partial Pressures** states that the total pressure of a mixture of gases is equal to the sum of all of the partial pressures of the component gases. Dalton's Law can be expressed with the following equation:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$$

The figure below shows two gases that are in separate, equal-sized containers at the same temperature and pressure. Each exerts a different pressure, $P_1$ and $P_2$, reflective of the number of particles in the container. On the right, the two gases are combined into the same container, with no volume change. The total pressure of the gas mixture is equal to the sum of the individual pressures. If $P_1 = 300\ \text{mm Hg}$ and $P_2 = 500\ \text{mm Hg}$, then $P_{\text{total}} = 800\ \text{mm Hg}$.

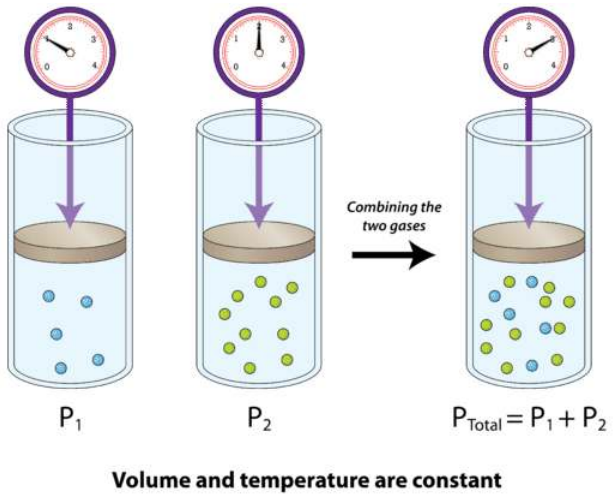



Figure 7.8.1: Dalton's Law states that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

## Collecting Gases Over Water

You need to do a lab experiment where hydrogen gas is generated. In order to calculate the yield of gas, you have to know the pressure inside the tube where the gas is collected. But how can you get a barometer in there? Very simple: you don't. All you need

is the atmospheric pressure in the room. As the gas pushes out the water, it is pushing against the atmosphere, so the pressure inside is equal to the pressure outside.

## Gas Collection by Water Displacement

Gases that are produced in laboratory experiments are often collected by a technique called **water displacement** (Figure 7.8.2). A bottle is filled with water and placed upside-down in a pan of water. The reaction flask is fitted with rubber tubing, which is then fed under the bottle of water. As the gas is produced in the reaction flask, it exits through the rubber tubing and displaces the water in the bottle. When the bottle is full of the gas, it can be sealed with a lid.



Figure 7.8.2: A gas produced in a chemical reaction can be collected by water displacement.

Because the gas is collected over water, it is not pure, but is mixed with vapor from the evaporation of the water. Dalton's Law can be used to calculate the amount of the desired gas by subtracting the contribution of the water vapor.

$$P_{\text{Total}} = P_g + P_{H_2O}$$

where $P_g$ is the pressure of the desired gas, which can be solved for:

$$P_g = P_{Total} - P_{H_2O}$$

In order to solve a problem, it is necessary to know the vapor pressure of water at the temperature of the reaction (see table below). The sample problem illustrates the use of Dalton's Law when a gas is collected over water.

Table 7.8.1: Vapor Pressure of Water (mm Hg) at Selected Temperatures (°C)

| 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4.58 | 6.54 | 9.21 | 12.79 | 17.54 | 23.76 | 31.82 | 42.18 | 55.32 | 71.88 | 92.51 | 118.04 | 149.38 |

### Example 14.14.1

A certain experiment generates 2.58 L of hydrogen gas, which is collected over water. The temperature is 20°C and the atmospheric pressure is 98.60 kPa. Find the volume that the dry hydrogen would occupy at STP.

**Solution**

*Step 1: List the known quantities and plan the problem.*

Known

- $V_{\text{Total}} = 2.58\ \text{L}$
- $T = 20°\text{C} = 293\ \text{K}$
- $P_{\text{Total}} = 98.60\ \text{kPa} = 739.7\ \text{mm Hg}$

Unknown

- $V_{H_2}$ at STP $=?\ \text{L}$

The atmospheric pressure is converted from kPa to mm Hg in order to match units with the table. The sum of the pressures of the hydrogen and the water vapor is equal to the atmospheric pressure. The pressure of the hydrogen is found by subtraction. Then, the volume of the gas at STP can be calculated by using the combined gas law.

*Step 2: Solve.*

$$P_{H_2} = P_{\text{Total}} - P_{H_2O}$$
$$= 739,7 \text{ mm Hg} - 17.54 \text{ mm Hg}$$
$$= 722.2 \text{ mm Hg}$$

Now the combined gas law is used, solving for $V_2$, the volume of hydrogen at STP.

$$V_2 = \frac{P_1 \times V_1 \times T_2}{P_2 \times T_1}$$
$$= \frac{722.2 \text{ mm Hg} \times 2.58 \text{ L} \times 273 \text{ K}}{760 \text{ mm Hg} \times 293 \text{ K}}$$
$$= 2.28 \text{ L } H_2$$

*Step 3: Think about your result.*

If the hydrogen gas were to be collected at STP and without the presence of the water vapor, its volume would be **2.28 L**. This is less than the actual collected volume because some of that is water vapor. The conversion using STP is useful for stoichiometry purposes.

## Summary

- Dalton's Law of Partial Pressures states that the total pressure in a system is equal to the sum of the partial pressures of the gases present.
- The vapor pressure due to water in a sample can be corrected for, in order to get the true value for the pressure of the gas.

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# CHAPTER OVERVIEW

## 8: Energy and Energy Changes


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# 8.1: Energy

**Learning Objectives**

- Define heat and work.
- Distinguish between kinetic energy and potential energy.
- State the law of conservation of matter and energy.

Just like matter, energy is a term that we are all familiar with and use on a daily basis. Before you go on a long hike, you eat an *energy* bar; every month, the *energy* bill is paid; on TV, politicians argue about the *energy* crisis. But what is energy? If you stop to think about it, energy is very complicated. When you plug a lamp into an electric socket, you see energy in the form of light, but when you plug a heating pad into that same socket, you only feel warmth. Without energy, we couldn't turn on lights, we couldn't brush our teeth, we couldn't make our lunch, and we couldn't travel to school. In fact, without energy, we couldn't even wake up because our bodies require energy to function. We use energy for every single thing that we do, whether we are awake or asleep.

## Ability to Do Work or Produce Heat

When we speak of *using* energy, we are really referring to *transferring* energy from one place to another. When you use energy to throw a ball, you transfer energy from your body to the ball, and this causes the ball to fly through the air. When you use energy to warm your house, you transfer energy from the furnace to the air in your home, and this causes the temperature in your house to rise. Although energy is used in many kinds of different situations, all of these uses rely on energy being transferred in one of two ways. Energy can be transferred as *heat* or as *work*.

When scientists speak of ***heat***, they are referring to energy that is transferred from an object with a higher temperature to an object with a lower temperature, as a result of the temperature difference. Heat will "flow" from the hot object to the cold object until both end up at the same temperature. When you cook with a metal pot, you witness energy being transferred in the form of heat. Initially, only the stove element is hot—the pot and the food inside the pot are cold. As a result, heat moves from the hot stove element to the cold pot. After a while, enough heat is transferred from the stove to the pot, raising the temperature of the pot and all of its contents (Figure **8.1.1**).



Figure **8.1.1**: Energy is transferred as heat from the hot stove element to the cooler pot until the pot and its contents become just as hot as the element. The energy that is transferred into the pot as heat is then used to cook the food.

Heat is only one way in which energy can be transferred. Energy can also be transferred as **work**. The scientific definition of work is *force (any push or pull) applied over a distance*. When you push an object and cause it to move, you do work, and you transfer some of *your* energy to the object. At this point, it's important to warn you of a common misconception. Sometimes we think that the amount of work done can be measured by the amount of effort put in. This may be true in everyday life, but it is not true in science. By definition, scientific work requires that force be applied *over a distance*. It does not matter how hard you push or how hard you pull. If you have not moved the object, you haven't done any work.

So far, we've talked about the two ways in which energy can be transferred from one place, or object, to another. Energy can be transferred as heat, and energy can be transferred as work. But the question still remains—*what IS energy*?

## Kinetic Energy

Machines use energy, our bodies use energy, energy comes from the sun, energy comes from volcanoes, energy causes forest fires, and energy helps us to grow food. With all of these seemingly different types of energy, it's hard to believe that there are really only two different *forms* of energy: kinetic energy and potential energy. **Kinetic energy** is energy associated with motion. When an object is moving, it has kinetic energy. When the object stops moving, it has no kinetic energy. While all moving objects have kinetic energy, not all moving objects have the same amount of kinetic energy. The amount of kinetic energy possessed by an object is determined by its mass and its speed. The heavier an object is and the faster it is moving, the more kinetic energy it has.

Kinetic energy is very common, and it's easy to spot examples of it in the world around you. Sometimes we even try to capture kinetic energy and use it to power things like our home appliances. If you are from California, you might have driven through the Tehachapi Pass near Mojave or the Montezuma Hills in Solano County and seen the windmills lining the slopes of the mountains (Figure 8.1.2). These are two of the larger wind farms in North America. As wind rushes along the hills, the kinetic energy of the moving air particles turns the windmills, trapping the wind's kinetic energy so that people can use it in their houses and offices.



Figure 8.1.2: A wind farm in Solano County harnesses the kinetic energy of the wind. (CC BY-SA 3.0 Unported; BDS2006 at Wikipedia)

## Potential Energy

**Potential energy** is *stored* energy. It is energy that remains available until we choose to use it. Think of a battery in a flashlight. If left on, the flashlight battery will run out of energy within a couple of hours, and the flashlight will die. If, however, you only use the flashlight when you need it, and turn it off when you don't, the battery will last for days or even months. The battery contains a certain amount of energy, and it will power the flashlight for a certain amount of time, but because the battery stores *potential* energy, you can choose to use the energy all at once, or you can save it and only use a small amount at a time.

Any stored energy is potential energy. There are a lot of different ways in which energy can be stored, and this can make potential energy very difficult to recognize. In general, an object has potential energy because of its *position relative to another object*. For example, when a rock is held above the earth, it has potential energy because of its position relative to the ground. This is *potential energy* because the energy is *stored* for as long as the rock is held in the air. Once the rock is dropped, though, the stored energy is released as kinetic energy as the rock falls.

## Chemical Energy

There are other common examples of potential energy. A ball at the top of a hill stores potential energy until it is allowed to roll to the bottom. When two magnets are held next to one another, they store potential energy too. For some examples of potential energy, though, it's harder to see how "position" is involved. In chemistry, we are often interested in what is called **chemical potential energy**. Chemical potential energy is energy stored in the atoms, molecules, and chemical bonds that make up matter. How does this depend on position?

As you learned earlier, the world, and all of the chemicals in it are made up of atoms and molecules. These store potential energy that is dependent on their positions relative to one another. Of course, you can't see atoms and molecules. Nevertheless, scientists do know a lot about the ways in which atoms and molecules interact, and this allows them to figure out how much potential energy

is stored in a specific quantity (like a cup or a gallon) of a particular chemical. *Different chemicals have different amounts of potential energy* because they are made up of different atoms, and those atoms have different positions relative to one another.

> Since different chemicals have different amounts of potential energy, scientists will sometimes say that potential energy depends not only on ***position***, but also on ***composition***. Composition affects potential energy because it determines which molecules and atoms end up next to one another. For example, the total potential energy in a cup of pure water is different than the total potential energy in a cup of apple juice, because the cup of water and the cup of apple juice are *composed* of different amounts of different chemicals.

At this point, you may wonder just how useful chemical potential energy is. If you want to release the potential energy stored in an object held above the ground, you just drop it. But how do you get potential energy out of chemicals? It's actually not difficult. Use the fact that different chemicals have *different amounts of potential energy*. If you start with chemicals that have a lot of potential energy and allow them to react and form chemicals with less potential energy, all the extra energy that was in the chemicals at the beginning, but not at the end, is released.

## Units of Energy

Energy is measured in one of two common units: the calorie and the joule. The joule (**J**) is the SI unit of energy. The calorie is familiar because it is commonly used when referring to the amount of energy contained within food. A **calorie** (**cal**) is the quantity of heat required to raise the temperature of 1 gram of water by $1°C$. For example, raising the temperature of $100\ g$ of water from $20°C$ to $22°C$ would require $100 \times 2 = 200\ cal$.

Calories contained within food are actually kilocalories (**kcal**). In other words, if a certain snack contains 85 food calories, it actually contains $85\ kcal$ or $85,000\ cal$. In order to make the distinction, the dietary calorie is written with a capital C.

$$1\ \text{kilocalorie} = 1\ \text{Calorie} = 1000\ \text{calories}$$

To say that the snack "contains" 85 Calories means that $85\ kcal$ of energy are released when that snack is processed by your body.

Heat changes in chemical reactions are typically measured in joules rather than calories. The conversion between a joule and a calorie is shown below.

$$1\ J = 0.2390\ cal \text{ or } 1\ cal = 4.184\ J$$

We can calculate the amount of heat released in kilojoules when a 400 Calorie hamburger is digested.

$$400\ Cal = 400\ kcal \times \frac{4.184\ kJ}{1\ kcal} = 1.67 \times 10^3\ kJ$$

## Summary

- Any time we use energy, we transfer energy from one object to another.
- Energy can be transferred in one of two ways: as heat, or as work.
- Heat is the term given to energy that is transferred from a hot object to a cooler object due to the difference in their temperatures.
- Work is the term given to energy that is transferred as a result of a force applied over a distance.
- Energy comes in two fundamentally different forms: kinetic energy and potential energy.
- Kinetic energy is the energy of motion.
- Potential energy is stored energy that depends on the position of an object relative to another object.
- Chemical potential energy is a special type of potential energy that depends on the positions of different atoms and molecules relative to one another.
- Chemical potential energy can also be thought of according to its dependence on chemical composition.
- Energy can be converted from one form to another. The total amount of mass and energy in the universe is conserved.

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# 8.2: Heat and Temperature

**Learning Objectives**

- To relate heat transfer to temperature change.
- Memorize temperature equations for Celsius, Fahrenheit and Kelvin conversions.
- Understand how body temperature can vary.

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being "hot." Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as "cold." In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

## Temperature Scales

Temperature is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees. There are three scales used for reporting temperatures. Figure **8.2.1** compares the three temperature scales: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

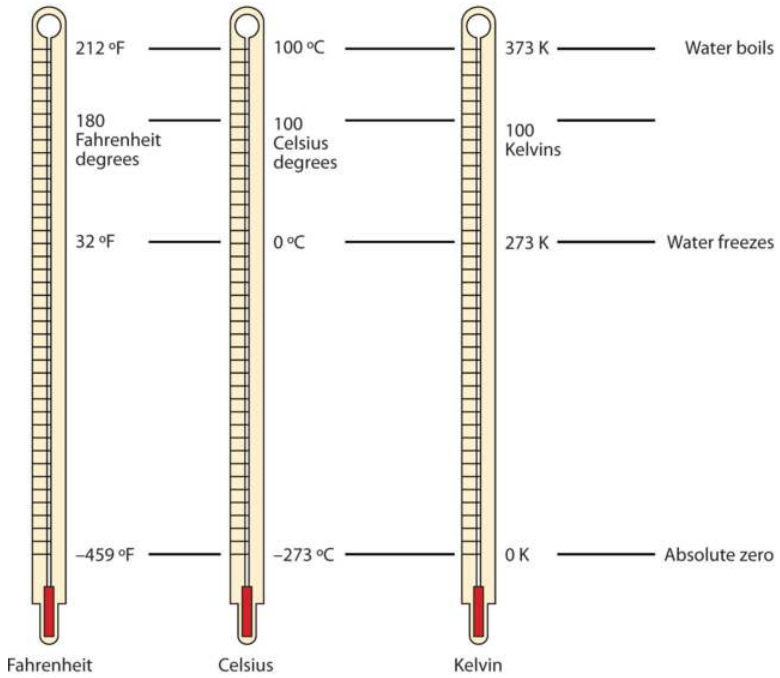



Figure **8.2.1**: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales. These thermometers have a red-colored liquid which contains alcohol and food coloring. Silver looking thermometers contain mercury, which is a neurotoxin.

In the United States, the commonly used temperature scale is the *Fahrenheit scale* (symbolized by °F and spoken as "degrees Fahrenheit"). On this scale, the freezing point of liquid water (the temperature at which liquid water turns to solid ice) is 32 °F, and the boiling point of water (the temperature at which liquid water turns to steam) is 212 °F.

Science also uses other scales to express temperature. For example, the Celsius scale (symbolized by °C and spoken as "degrees Celsius") defines 0°C as the freezing point of water and 100 °C as the boiling point of water. This scale is divided into 100

divisions between these two landmarks and extended higher and lower as well. By comparing the Fahrenheit and Celsius scales, a conversion between the two scales can be determined:

$$^{\circ}C = (^{\circ}F - 32) \times \frac{5}{9} \tag{8.2.1}$$

$$^{\circ}F = \left(^{\circ}C \times \frac{9}{5}\right) + 32 \tag{8.2.2}$$

Note that science uses the Celsius and Kelvin scales almost exclusively; virtually no practicing chemist expresses laboratory-measured temperatures with the Fahrenheit scale. (In fact, the United States is one of the few countries in the world that still uses the Fahrenheit scale on a daily basis. People driving near the borders of Canada or Mexico may pick up local radio stations on the other side of the border that express the daily weather in degrees Celsius, so do not get confused by their weather reports.)

### Example 8.2.1: Conversions

a. What is 98.6°F in degrees Celsius?
b. What is 25.0°C in degrees Fahrenheit?

**Solution**

a. Using Equation 8.2.1, we have

$$\begin{aligned} ^{\circ}C &= (98.6 - 32) \times \frac{5}{9} \\ &= 66.6 \times \frac{5}{9} \\ &= 37.0^{\circ}C \end{aligned}$$

b. Using Equation 8.2.2, we have

$$\begin{aligned} ^{\circ}F &= (25.0 \times \frac{9}{5}) + 32 \\ &= 45.0 + 32 \\ &= 77.0^{\circ}F \end{aligned}$$

For more examples of how to perform these types of problems, click on this video to see your professor in action.

### Exercise 8.2.1

a. Convert 0°F to degrees Celsius.
b. Convert 212°C to degrees Fahrenheit.

**Answer a**

−17.8°C

**Answer b**

414°F

The fundamental unit of temperature in SI is the Kelvin (K). The Kelvin temperature scale (note that the name of the scale capitalizes the word *Kelvin*, but the unit itself is lowercase) uses degrees that are the same size as the Celsius degree, but the numerical scale is shifted up by 273.15 units. That is, the conversion between the Kelvin and Celsius scales is as follows:

$$K =^{\circ} C + 273.15 \tag{8.2.3}$$

For most purposes, it is acceptable to use 273 instead of 273.15 in Equation 8.2.3.

Note that the Kelvin scale does not use the word *degrees*; a temperature of 295 K is spoken of as “two hundred ninety-five kelvin” and not “two hundred ninety-five degrees Kelvin.”

The reason that the Kelvin scale is defined this way is that there exists a minimum possible temperature called absolute zero (zero Kelvin). The Kelvin temperature scale is set so that 0 K is absolute zero, and the temperature is counted upward from there. Normal room temperature is about 295 K, as seen in the following example.

### Example 8.2.2: Room Temperature

If the normal room temperature is 72.0°F, what is room temperature in degrees Celsius and kelvin?

**Solution**

First, we use Equation 8.2.1 to determine the temperature in degrees Celsius:

$$\begin{aligned} ^\circ C &= (72.0 - 32) \times \frac{5}{9} \\ &= 40.0 \times \frac{5}{9} \\ &= 22.2^\circ C \end{aligned}$$

Then we use Equation 8.2.3 to determine the temperature in the Kelvin scale:

$$\begin{aligned} K &= 22.2^\circ C + 273.15 \\ &= 295.4 K \end{aligned}$$

So, room temperature is about 295 K.

### Health Application: Body temperature

Normal body temperature is defined as being 98.6°F (+/- 1.0°F). To determine body temperature, thermometers can be placed inside or on the surface of the body. The two best methods of obtaining body temperature are placing the thermometer either under the tongue or inside the rectum. Typically, children are capable of holding a thermometer in their mouths around the age of four (have fun before that age).

Fever is defined as body temperature being above 100°F (adults). High fever status occurs at and above 104°F. For adults, these adults should seek medical attention immediately if the fever exceeds 104°F. For children, these values are much lower.

Hyperthermia (inability of the body to regulate heat) occurs when normal body temperature is exceeded. Conditions that can cause hyperthermia are fever (infection), heat stroke, thyroid disorders, heart attack, or traumatic injury. Medications for cancer, arthritis, and thyroid patients can cause the body temperature to rise. Symptoms of hyperthermia include sweating, confusion, nausea, and dizziness.

Hypothermia (exposure to cold environments) occurs when normal body temperature dips below 95.0°F. When this occurs, the affected person(s) should seek immediate medical attention. During hypothermia, the body has problems producing heat. Medical conditions like diabetes, infection, and thyroid dysfunction can cause hypothermia. Watch this video of American Marines attempting to survive extreme environments. Symptoms of this condition involve shivering, confusion, and sluggish behavior.

Treating hyperthermia could involve hydrating a patient. If a fever is due to infection, analgesics (like Tylenol, Advil, aspirin, or Aleve) can help alleviate fever. Placing someone in a cool bath can also relieve symptoms.

To combat hypothermia, one must remove wet clothing, redress in warm materials, and participate in physical movement.

## Heat transfer

Heat is a familiar manifestation of energy. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from

our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

Suppose we consider the transfer of heat from the opposite perspective—namely, what happens to a system that gains or loses heat? Generally, the system’s temperature changes. (We will address a few exceptions later.) The greater the original temperature difference, the greater the transfer of heat, and the greater the ultimate temperature change. The relationship between the amount of heat transferred and the temperature change can be written as

$$\text{heat} \propto \Delta T \tag{8.2.4}$$

where ∝ means “is proportional to” and **$\Delta T$ is the change in temperature of the system**. Any change in a variable is always defined as “the final value minus the initial value” of the variable, so $\Delta T$ is $T_{\text{final}} - T_{\text{initial}}$. In addition, the greater the mass of an object, the more heat is needed to change its temperature. We can include a variable representing mass ($m$) to the proportionality as follows:

$$\text{heat} \propto m\Delta T \tag{8.2.5}$$

To change this proportionality into an equality, we include a proportionality constant. The proportionality constant is called the specific heat and is commonly symbolized by $c$:

$$\text{heat} = mc\Delta T \tag{8.2.6}$$

Every substance has a characteristic **specific heat**, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express $\Delta T$. The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°C. Table 8.2.1 lists the specific heats for various materials.

Table 8.2.1: Specific Heats of Selected Substances

| Substance | c (cal/g•°C) |
|---|---|
| aluminum (Al) | 0.215 |
| aluminum oxide ($Al_2O_3$) | 0.305 |
| benzene ($C_6H_6$) | 0.251 |
| copper (Cu) | 0.092 |
| ethanol ($C_2H_6O$) | 0.578 |
| hexane ($C_6H_{14}$) | 0.394 |
| hydrogen ($H_2$) | 3.419 |
| ice [$H_2O(s)$] | 0.492 |
| iron (Fe) | 0.108 |
| iron(III) oxide ($Fe_2O_3$) | 0.156 |
| mercury (Hg) | 0.033 |
| oxygen ($O_2$) | 0.219 |
| sodium chloride (NaCl) | 0.207 |
| steam [$H_2O(g)$] | 0.488 |
| water [$H_2O(\ell)$] | 1.00 |

> *The proportionality constant c is sometimes referred to as the specific heat capacity or (incorrectly) the heat capacity.*

The *direction* of heat flow is not shown in heat = $mc\Delta T$. If energy goes into an object, the total energy of the object increases, and the values of heat $\Delta T$ are positive. If energy is coming out of an object, the total energy of the object decreases, and the values of heat and $\Delta T$ are negative.

### Example 8.2.3

What quantity of heat is transferred when a 150.0 g block of iron metal is heated from 25.0°C to 73.3°C? What is the direction of heat flow?

#### Solution

We can use Equation 8.2.6 to determine the amount of heat, but first we need to determine $\Delta T$. Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, $\Delta T$ is as follows:

$$\begin{aligned}\Delta T &= T_{final} - T_{initial} \\ &= 73.3^{o}C - 25.0^{o}C \\ &= 48.3^{o}C\end{aligned}$$

The mass is given as 150.0 g, and Table 8.2.1 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into Equation 8.2.6 and solve for amount of heat:

$$\text{heat} = (150.0\ \text{g})\left(0.108\ \frac{\text{cal}}{\text{g}\cdot{}^{\circ}\text{C}}\right)(48.3^{\circ}\text{C}) = 782\ \text{cal}$$

Note how the gram and °C units cancel algebraically, leaving only the calorie unit, which is a unit of heat. Because the temperature of the iron increases, energy (as heat) must be flowing *into* the metal.

### 8.2.3 Exercise

What quantity of heat is transferred when a 295.5 g block of aluminum metal is cooled from 128.0°C to 22.5°C? What is the direction of heat flow?

#### Answer

6,700 cal

### Example 8.2.4

A 10.3 g sample of a reddish-brown metal gave off 71.7 cal of heat as its temperature decreased from 97.5°C to 22.0°C. What is the specific heat of the metal? Can you identify the metal from the data in Table 8.2.1?

#### Solution

The question gives us the heat, the final and initial temperatures, and the mass of the sample. The value of $\Delta T$ is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0^{\circ}\text{C} - 97.5^{\circ}\text{C} = -75.5^{\circ}\text{C}$$

If the sample gives off 71.7 cal, it loses energy (as heat), so the value of heat is written as a negative number, −71.7 cal. Substitute the known values into heat = $mc\Delta T$ and solve for $c$:

$$-71.7\ \text{cal} = (10.3\ \text{g})(c)(-75.5^{\circ}\text{C})$$

$$c = \frac{-71.7\ \text{cal}}{(10.3\ \text{g})(-75.5^{\circ}\text{C})}$$

$$c = 0.0923\ \text{cal/g}\cdot{}^{\circ}\text{C}$$

This value for specific heat is very close to that given for copper in Table 8.2.1.

### 8.2.4 Exercise

A 10.7 g crystal of sodium chloride (NaCl) had an initial temperature of 37.0°C. What is the final temperature of the crystal if 147 cal of heat were supplied to it?

**Answer**

103.4°C

Notice that water has a very high specific heat compared to most other substances. Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see table above). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.



Figure **8.2.2**: This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.

## Summary

- Heat transfer is related to temperature change.
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by **1°C**.

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# 8.2.1: Specific Heat Calculations

**Learning Objectives**

- Define specific heat.
- Use specific heat in energy calculations.

Water has a high capacity for absorbing heat. In a car radiator, it serves to keep the engine cooler than it would otherwise run. As the water circulates through the engine, it absorbs heat from the engine block. When it passes through the radiator, the cooling fan and the exposure to the outside environment allow the water to cool somewhat before it makes another passage through the engine.

## Specific Heat Calculations

The specific heat of a substance can be used to calculate the temperature change that a given substance will undergo when it is either heated or cooled. The equation that relates heat ($q$) to specific heat ($c_p$), mass ($m$), and temperature change ($\Delta T$) is shown below.

$$q = c_p \times m \times \Delta T$$

The heat that is either absorbed or released is measured in joules. The mass is measured in grams. The change in temperature is given by $\Delta T = T_f - T_i$, where $T_f$ is the final temperature and $T_i$ is the initial temperature.

**Example 8.2.1.1**

A $15.0\ \text{g}$ piece of cadmium metal absorbs $134\ \text{J}$ of heat while rising from $24.0^\circ\text{C}$ to $62.7^\circ\text{C}$. Calculate the specific heat of cadmium.

**Solution**

*Step 1: List the known quantities and plan the problem.*

Known

- Heat $= q = 134\ \text{J}$
- Mass $= m = 15.0\ \text{g}$
- $\Delta T = 62.7^\circ\text{C} - 24.0^\circ\text{C} = 38.7^\circ\text{C}$

Unknown

The specific heat equation can be rearranged to solve for the specific heat.

*Step 2: Solve.*

$$c_p = \frac{q}{m \times \Delta T} = \frac{134\ \text{J}}{15.0\ \text{g} \times 38.7^\circ\text{C}} = 0.231\ \text{J/g}^\circ\text{C}$$

*Step 3: Think about your result.*

The specific heat of cadmium, a metal, is fairly close to the specific heats of other metals. The result has three significant figures.

Since most specific heats are known, they can be used to determine the final temperature attained by a substance when it is either heated or cooled. Suppose that $60.0\ \text{g}$ of water at $23.52^\circ\text{C}$ was cooled by the removal of $813\ \text{J}$ of heat. The change in temperature can be calculated using the specific heat equation:

$$\Delta T = \frac{q}{c_p \times m} = \frac{813\ \text{J}}{4.18\ \text{J/g}^\circ\text{C} \times 60.0\ \text{g}} = 3.24^\circ\text{C}$$

Since the water was being cooled, the temperature decreases. The final temperature is:

$$T_f = 23.52^\circ\text{C} - 3.24^\circ\text{C} = 20.28^\circ\text{C}$$

## Summary

- The specific heat of a substance can be used to calculate the temperature change of the substance when it is heated or cooled.
- Specific heat calculations are illustrated.

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# 8.3: Bond Energies and Chemical Reactions

**Learning Objectives**

The Learning Objectives of this Module are to:

- Define *bond energy*.
- Describe enthalpy and energy changes in a reaction.

What happens when you take a basketball, place it halfway up a playground slide, and then let it go? The basketball rolls down the slide. What happens if you do it again? Does the basketball roll down the slide? It should.

If you were to perform this experiment over and over again, do you think the basketball would ever roll *up* the slide? Probably not. Why not? Well, for starters, in all of our experience, the basketball has always moved to a lower position when given the opportunity. The gravitational attraction of Earth exerts a force on the basketball, and given the chance, the basketball will move down. We say that the basketball is going to a lower *gravitational potential energy*. The basketball can move up the slide, but only if someone exerts some effort (that is, work) on the basketball. A general statement, based on countless observations over centuries of study, is that all objects tend to move spontaneously to a position of minimum energy unless acted on by some other force or object.

## Bond Energy

A similar statement can be made about atoms in compounds. Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.* In making compounds, atoms act like a basketball on a playground slide; they move in the direction of decreasing energy.

We can reverse the process, just as with the basketball. If we put energy into a molecule, we can cause its bonds to break, separating a molecule into individual atoms. Bonds between certain specific elements usually have a characteristic energy, called the bond energy, that is needed to break the bond. The same amount of energy was liberated when the atoms made the chemical bond in the first place. The term *bond energy* is usually used to describe the strength of interactions between atoms that make covalent bonds. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. The C=C bond is stronger than C-C (as discussed in relation to bond length in Section 4.4). For atoms in ionic compounds attracted by opposite charges, the term lattice energy is used. For now, we will deal with covalent bonds in molecules.

Although each molecule has its own characteristic bond energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. Table **8.3.1** lists the approximate bond energies of various covalent bonds.

Table **8.3.1**: Approximate Bond Energies

| Bond | Bond Energy (kcal/mol) |
|---|---|
| C–H | 100 |
| C–O | 86 |
| C=O | 190 |
| C–N | 70 |
| C–C | 85 |
| C=C | 145 |
| C≡C | 200 |
| N–H | 93 |
| H–H | 105 |
| Br-Br | 46 |
| Cl–Cl | 58 |
| O–H | 110 |
| O=O | 119 |
| H–Br | 87 |
| H–Cl | 103 |

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*. The enthalpy change, for a given reaction can be calculated using the bond energy values from Table **8.3.1**.

## Enthalpy Change or Heat of Reaction, Δ*H*

Energy changes in chemical reactions are usually measured as changes in enthalpy. In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

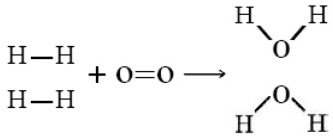
$$\text{enthalpy change} \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

The ≈ sign is used because we are adding together *average* bond energies (i.e., over many different molecules). Hence, this approach does not give exact values for the enthalpy change, Δ*H*.

Let's consider the reaction of 2 mols of hydrogen gas ($H_2$) with 1 mol of oxygen gas ($O_2$) to give 2 mol water:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

or shown graphically:



with these average bond energies involved:

- **H–H** = 105 kcal/mol
- **O=O** = 119 kcal/mol

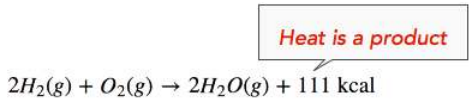
- **O–H** = 110 kcal/mol

In this reaction, 2 H–H bonds and 1 O=O bonds are broken, while 4 O–H bonds (two for each $H_2O$) are formed. The energy changes can be tabulated and calculated as follows:

| Bonds Broken (kcal/mol) | | Bonds Formed (kcal/mol) | |
|---|---|---|---|
| 2 H–H | 2 mol x 105 kcal/mol = 210 kcal | 4 O–H | 4 mols x 110 kcal/mol = 440 kcal |
| 1 O=O | 1 mol x 119 kcal/mol = 119 kcal | | |
| | **Total** = 329 kcal | | **Total** = 440 kcal |

$$\begin{aligned}\Delta H &\approx \sum(\text{bonds broken}) - \sum(\text{bonds formed}) \\ &\approx 329\ \text{kcal} - 440\ \text{kcal} \\ &\approx -111\ \text{kcal}\end{aligned}$$

The enthalpy change (ΔH) of the reaction is approximately −111 kcal/mol. This means that bonds in the products (440 kcal) are stronger than the bonds in the reactants (329 kcal) by about 111 kcal/mol. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes. This excess energy is **released** as heat. Hence, we can re-write the reaction with the heat released (111 kcal) on the **product side** of the equation, as follows:




We can also re-write the reaction equation with the ΔH information (see below). Note that an **exothermic** reaction has a **negative ΔH** value.

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \qquad \Delta H = -111\ \text{kcal}$$

**Example 8.3.1**

What is the enthalpy change for this reaction?

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

### Solution

Step 1- First look at the equation and identify which bonds exist on in the reactants (bonds broken).

- one H-H bond and
- one Br-Br bond

Step 2- Do the same for the products (bonds formed)

- two H-Br bonds

Step 3- Identify the bond energies of these bonds from Table **8.3.1**:

- H-H bonds: 105 kcal/mol
- Br-Br bonds: 46 kcal/mol

Step 4- Set up the table (see below) and apply the formula for enthalpy change.

| Bonds Broken (kcal/mol) | | Bonds Formed (kcal/mol) | |
|---|---|---|---|
| 1 H–H | 1 mol x 105 kcal/mol = 105 kcal | 2 H–*Br* | 2 mols x 87 kcal/mol = 174 kcal |
| 1 Br–Br | 1 mol x 46 kcal/mol = 46 kcal | | |
| | **Total** = 151 kcal | | **Total** = 174 kcal |

$$\Delta H \approx 151\ \text{kcal} - 174\ \text{kcal}$$
$$\approx -23\ \text{kcal}$$

## 8.3.1 Exercise

Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

Is the reaction written above exothermic or endothermic? Explain.

**Answer**

ΔH = −43 kcal

# Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Energy is required to break bonds. Energy is released when chemical bonds are formed because atoms become more stable.

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# 8.4: Exothermic and Endothermic Reactions

**Learning Objectives**

- Define endothermic and exothermic reactions.
- Determine if a chemical process is exothermic or endothermic.
- Use or interpret energy diagrams to describe energy changes in a reaction.

## Endothermic and Exothermic Reactions

Endothermic and exothermic reactions can be thought of as having energy as either a reactant of the reaction or a product. **Endothermic** reactions *require* energy, so energy is a reactant. Heat flows from the surroundings to the system (reaction mixture) and the enthalpy of the system increases ($\Delta H$ is positive). As discussed in the previous section, heat is released (considered a product) in an **exothermic** reaction, and the enthalpy of the system decreases ($\Delta H$ is negative).

In the course of an **endothermic** process, the system gains heat from the surroundings and so the **temperature of the surroundings decreases (gets cold).** A chemical reaction is **exothermic** if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, **the temperature of the surroundings increases.** See Figure 8.4.1.

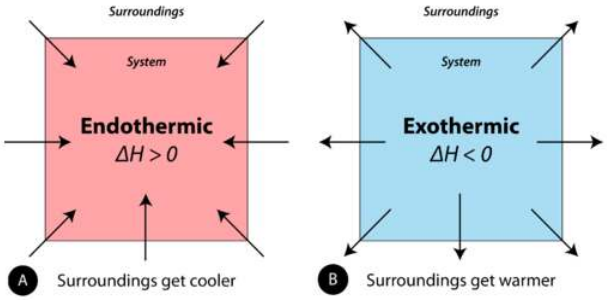



Figure 8.4.1: (A) Endothermic reaction. (B) Exothermic reaction.

**Endothermic Reaction**: When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. Because the heat is absorbed by the system, the 177.8 kJ is written as a **reactant**. The **$\Delta H$ is positive** for an endothermic reaction.

Heat is a reactant

$$CaCO_3\,(s) + 177.8\ \text{kJ} \rightarrow CaO\,(s) + CO_2\,(g)$$

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g) \quad \Delta H = +177.8\ \text{kJ} \tag{8.4.1}$$

**Exothermic Reaction**: When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of 1 mol of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation in two ways. First, the amount of heat released can be written in the **product** side of the reaction. Another way is to write the **heat of reaction** ($\Delta H$) information with a **negative** sign, −890.4 kJ.

Heat is a product

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + 890.4\ \text{kJ}$$

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) \quad \Delta H = -890.4\ \text{kJ} \tag{8.4.2}$$

**Example 8.4.2**

Is each chemical reaction exothermic or endothermic?

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

**Solution**

a. Because energy (213 kcal) is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.
b. Because energy (45 kcal) is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

**Exercise 8.4.2**

Is each chemical reaction exothermic or endothermic?

a. $H_2(g) + F_2(g) \rightarrow 2HF\ (g) + 130$ kcal
b. $2C(s) + H_2(g) + 5.3$ kcal $\rightarrow C_2H_2(g)$

**Answer**

a. The energy (130 kcal) is produced, hence the reaction is exothermic

b. The energy (5.3 kcal) is supplied or absorbed to react, hence, the reaction is endothermic

## Energy Diagrams

Endothermic and exothermic reactions can be visually represented by *energy-level diagrams* like the ones in **Figure 8.4.2**. In endothermic reactions, the reactants have higher bond energy (stronger bonds) than the products. **Strong bonds have lower potential energy than weak bonds**. Hence, the **energy of the reactants is lower than that of the products**. This type of reaction is represented by an "uphill" energy-level diagram shown in Figure 8.4.2*A*. For an endothermic chemical reaction to proceed, the reactants must absorb energy from their environment to be converted to products.

In an exothermic reaction, the bonds in the product have higher bond energy (stronger bonds) than the reactants. In other words, the **energy of the products is lower than the energy of the reactants,** hence is energetically downhill, shown in Figure 8.4.2*B*. Energy is given off as reactants are converted to products. The energy given off is usually in the form of heat (although a few reactions give off energy as light). In the course of an exothermic reaction, heat flows from the system to its surroundings, and thus, gets warm.

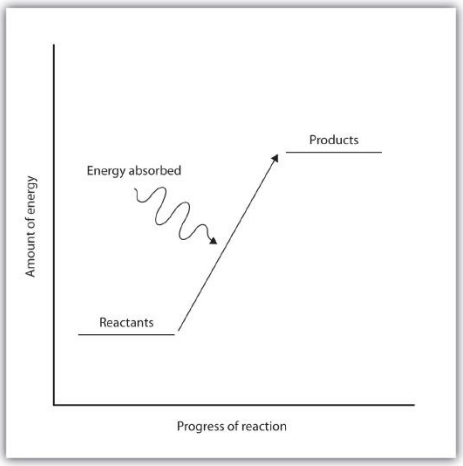



Figure 8.4.2A: Endothermic Reactions

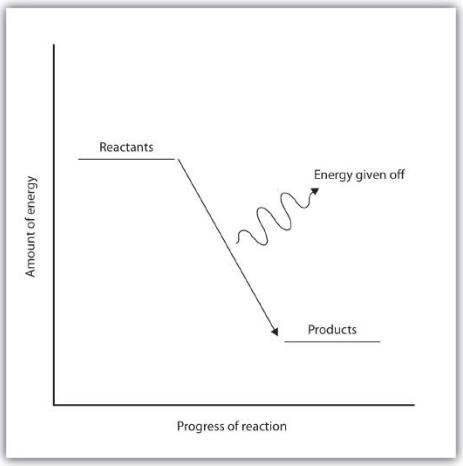



Figure 8.4.2B: Exothermic Reactions

Table 8.4.2: Endothermic and Exothermic Reactions

| Endothermic Reactions | Exothermic Reactions |
|---|---|
| Heat is absorbed by reactants to form products. | Heat is released. |
| Heat is absorbed from the surroundings; as a result, the surroundings get cold. | Heat is released by the reaction to surroundings; surroundings feel hot. |
| $\Delta H_{rxn}$ is positive | $\Delta H_{rxn}$ is negative |
| The bonds broken in the reactants are stronger than the bonds formed in the products | The bonds formed in the products are stronger than the bonds broken in the reactants |
| The reactants are lower in energy than the products | The products are lower in energy than the reactants |
| Represented by an "uphill" energy diagram | Represented by an "downhill" energy diagram |

## Concept Review Exercises

1. What is the connection between energy and chemical bonds?
2. Why does energy change during the course of a chemical reaction?
3. Two different reactions are performed in two identical test tubes. In reaction A, the test tube becomes very warm as the reaction occurs. In reaction B, the test tube becomes cold. Which reaction is endothermic and which is exothermic? Explain.
4. Classify "burning paper" as endothermic or exothermic processes.

## Answers

1. Chemical bonds have a certain energy that is dependent on the elements in the bond and the number of bonds between the atoms.
2. Energy changes because bonds rearrange to make new bonds with different energies.
3. Reaction A is exothermic because heat is leaving the system making the test tube feel hot. Reaction B is endothermic because heat is being absorbed by the system making the test tube feel cold.
4. "Burning paper" is exothermic because burning (also known as combustion) releases heat

## Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Energy is required to break bonds. Energy is released when chemical bonds are formed because atoms become more stable.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

## Exercises

1. Is a bond-breaking process exothermic or endothermic?
2. Is a bond-making process exothermic or endothermic?
3. Is each chemical reaction exothermic or endothermic?
    a. $2SnCl_2(s) + 33\ kcal \rightarrow Sn(s) + SnCl_4(s)$
    b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213\ kcal$
4. Is each chemical reaction exothermic or endothermic?
    a. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) + 137\ kJ$
    b. $C(s, graphite) + 1.9\ kJ \rightarrow C(s, diamond)$

## Answers

3. endothermic
4. exothermic
5.
    a. endothermic
    b. exothermic
6.
    a. exothermic
    b. endothermic

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# 8.5: Phase Changes and Energy Calculations

**Learning Objectives**

- Describe the energy changes associated with phase changes.
- Determine the heat associated with a phase change.
- Use heating and cooling curves to show energy changes.

Matter can exist in one of several different states, including a gas, liquid, or solid state. The amount of energy in molecules of matter determines the **state of matter**.

- A **gas** is a state of matter in which atoms or molecules have enough energy to move freely. The molecules come into contact with one another only when they randomly collide.
- A **liquid** is a state of matter in which atoms or molecules are constantly in contact but have enough energy to keep changing positions relative to one another.
- A **solid** is a state of matter in which atoms or molecules do not have enough energy to move. They are constantly in contact and in fixed positions relative to one another.

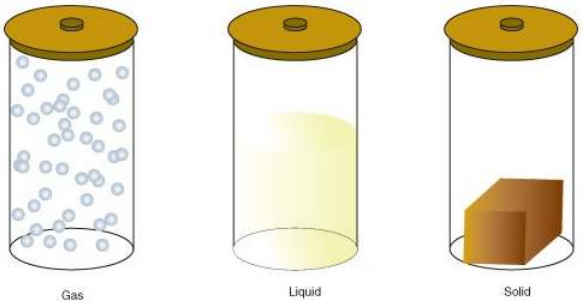



Figure **8.5.1**: States of Matter. All three containers contain a substance with the same mass, but the substances are in different states. In the left-hand container, the substance is a gas, which has spread to fill its container. It takes both the shape and volume of the container. In the middle container, the substance is a liquid, which has spread to take the shape of its container but not the volume. In the right-hand container, the substance is a solid, which takes neither the shape nor the volume of its container.

## Phase Changes

The following are the changes of state:

| | |
|---|---|
| Solid → Liquid | Melting or fusion |
| Liquid → Gas | Vaporization |
| Liquid → Solid | Freezing |
| Gas → Liquid | Condensation |
| Solid → Gas | Sublimation |

## Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure 8.6.18.6.1.

> *ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.*

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔHfusΔHfus), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔHvapΔHvap) of selected compounds are listed in Table 8.6.18.6.1.

Table 8.6.18.6.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

| Substance | Melting Point (°C) | $\Delta H_{fus}$ (kJ/mol) | Boiling Point (°C) | $\Delta H_{vap}$ (kJ/mol) |
|---|---|---|---|---|
| $N_2$ | −210.0 | 0.71 | −195.8 | 5.6 |
| HCl | −114.2 | 2.00 | −85.1 | 16.2 |
| $Br_2$ | −7.2 | 10.6 | 58.8 | 30.0 |
| $CCl_4$ | −22.6 | 2.56 | 76.8 | 29.8 |
| $CH_3CH_2OH$ (ethanol) | −114.1 | 4.93 | 78.3 | 38.6 |
| $CH_3(CH_2)_4CH_3$ (*n*-hexane) | −95.4 | 13.1 | 68.7 | 28.9 |
| $H_2O$ | 0 | 6.01 | 100 | 40.7 |
| Na | 97.8 | 2.6 | 883 | 97.4 |
| NaF | 996 | 33.4 | 1704 | 176.1 |

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

> *Less energy is needed to allow molecules to move past each other than to separate them totally.*

### ✔ Example 8.5.1

Label each of the following processes as endothermic or exothermic.

a. water boiling
b. ice forming on a pond

**Solution**

a. endothermic - you must put a pan of water on the stove and give it heat in order to get water to boil. Because you are adding heat/energy, the reaction is endothermic.
b. exothermic - think of ice forming in your freezer instead. You put water into the freezer, which takes heat out of the water, to get it to freeze. Because heat is being pulled out of the water, it is exothermic. Heat is leaving.

### 8.5.1 Exercise

Label each of the following processes as endothermic or exothermic.

a. water vapor condensing

b. gold melting

**Answer**

a. exothermic

b. endothermic

## Temperature Curves

The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

### Heating Curves

A phase change is a physical process in which a substance goes from one phase to another. Usually the change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The melting point is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The boiling point is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid or a liquid to a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water ($H_2O$) as an example. On the Celsius scale, $H_2O$ has a melting point of 0°C and a boiling point of 100°C. At 0°C, both the solid and liquid phases of $H_2O$ can coexist. However, if heat is added, some of the solid $H_2O$ will melt and turn into liquid $H_2O$. If heat is removed, the opposite happens: some of the liquid $H_2O$ turns into solid $H_2O$. A similar process can occur at 100°C: adding heat increases the amount of gaseous $H_2O$, while removing heat increases the amount of liquid $H_2O$ (Figure **8.5.1**).

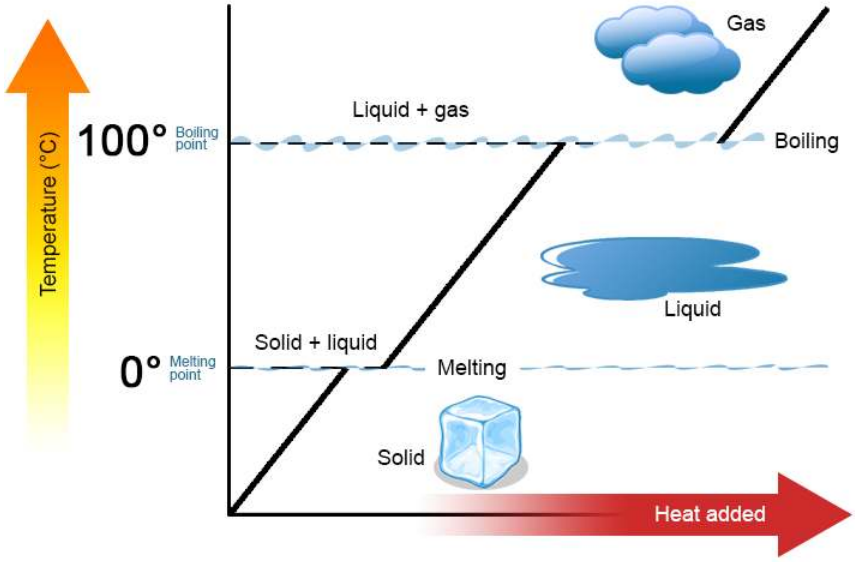



Figure **8.5.2**: Heating curve for water. As heat is added to solid water, the temperature increases until it reaches 0 °C, the melting point. At this point, the phase change, added heat goes into changing the state from a solid to liquid. Only when this phase change is complete, the temperature can increase. (CC BY 3.0 Unported; Community College Consortium for Bioscience Credentials).

Water is a good substance to use as an example because many people are already familiar with it. Other substances have melting points and boiling points as well.

Second, as shown in Figure **8.5.2**, **the temperature of a substance does not change** as the substance goes **from one phase to another**. In other words, phase changes are isothermal (isothermal means "constant temperature"). Again, consider $H_2O$ as an example. Solid water (ice) can exist at 0°C. If heat is added to ice at 0°C, some of the solid changes phase to make liquid, which is

also at 0°C. Remember, the solid and liquid phases of $H_2O$ can coexist at 0°C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion ($\Delta H_{fus}$) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. The heat of vaporization ($\Delta H_{vap}$) is the amount of heat per gram (or per mole) required for a phase change that occurs at the boiling point. If you know the total number of grams or moles of material, you can use the $\Delta H_{fus}$ or the $\Delta H_{vap}$ to determine the total heat being transferred for melting or solidification using these expressions:

$$\text{heat} = n \times \Delta H_{fus} \tag{8.5.1}$$

where $n$ is the number of moles and $\Delta H_{fus}$ is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{fus} \tag{8.5.2}$$

where $m$ is the mass in grams and $\Delta H_{fus}$ is expressed in energy/gram.

For the boiling or condensation, use these expressions:

$$\text{heat} = n \times \Delta H_{vap} \tag{8.5.3}$$

where $n$ is the number of moles) and $\Delta H_{vap}$ is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{vap} \tag{8.5.4}$$

where $m$ is the mass in grams and $\Delta H_{vap}$ is expressed in energy/gram.

Remember that a phase change depends on the direction of the heat transfer. If heat transfers in, solids become liquids, and liquids become solids at the melting and boiling points, respectively. If heat transfers out, liquids solidify, and gases condense into liquids. At these points, there are no changes in temperature as reflected in the above equations.

### Example 8.5.2

How much heat is necessary to melt 55.8 g of ice (solid $H_2O$) at 0°C? The heat of fusion of $H_2O$ is 79.9 cal/g.

#### Solution

We can use the relationship between heat and the heat of fusion (Equation **8.5.1**) to determine how many cal of heat are needed to melt this ice:

$$\text{heat} = \text{m} \times \Delta\text{H}_{\text{fus}}$$

$$\text{heat} = (55.8 \cancel{\text{g}}) \left( \frac{79.9 \text{ cal}}{\cancel{\text{g}}} \right) = 4,460 \text{ cal}$$

### Exercise 8.5.2

How much heat is necessary to vaporize 685 g of $H_2O$ at 100°C? The heat of vaporization of $H_2O$ is 540 cal/g.

**Answer**

$$\text{heat} = \text{m} \times \Delta\text{H}_{\text{vap}}$$

$$\text{heat} = (685 \cancel{\text{g}}) \left( \frac{540 \text{ cal}}{\cancel{\text{g}}} \right) = 370,000 \text{ cal}$$

## Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure **8.5.3** 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 **8.5.2**, 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.

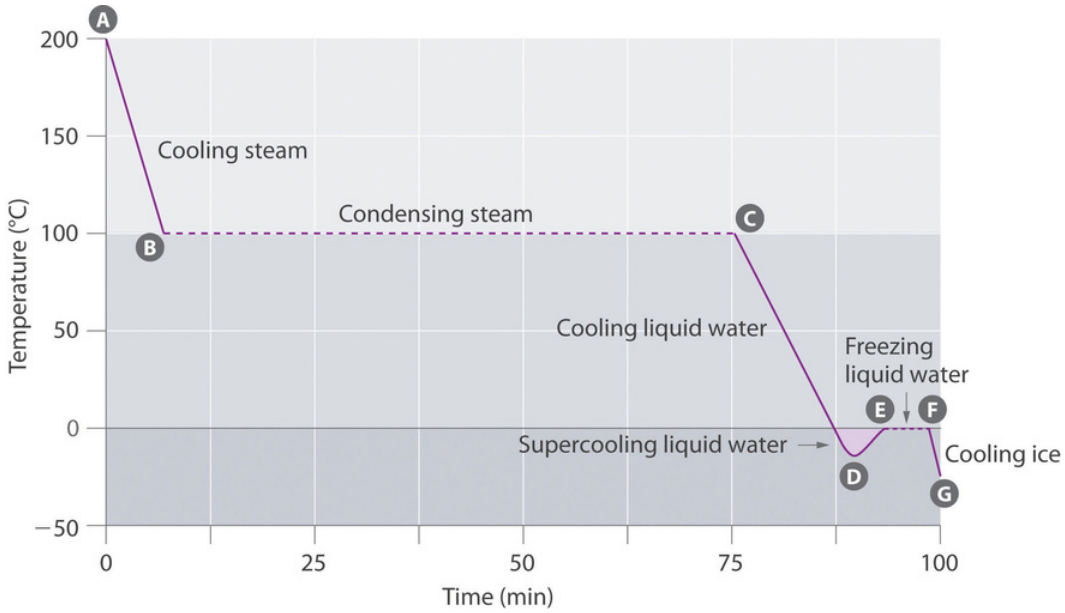



Figure 8.5.3: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

## Key Takeaway

- There is an energy change associated with any phase change.

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# 8.6: Phase Diagrams

**Learning Objectives**

- Describe phase diagrams.
- Identify the phase or phase change of a substance using a phase diagram.

Many rockets use a combination of kerosene and liquid oxygen for their fuel. Oxygen can be reduced to the liquid state either by cooling or by using high pressure. In the case of a rocket, since the oxygen is in a container essentially out in the open, maintaining a temperature of $-183°C$ (the boiling point of oxygen) is not very practical. However, high pressure can be used to force the oxygen into tanks, causing it to liquefy so that it can mix with the kerosene, and provide a powerful ignition to move the rocket.

## Phase Diagrams

The relationship among the solid, liquid, and vapor (gas) states of a substance can be shown as a function of temperature and pressure in a single diagram. A **phase diagram** is graph showing the conditions of temperature and pressure under which a substance exists in the solid, liquid, and gas phases. Examine the general phase diagram shown in the figure below. In each of the three colored regions of the diagram, the substance is in a single state (or phase). The dark lines that act as the boundary between those regions represent the conditions under which the two phases are in equilibrium.

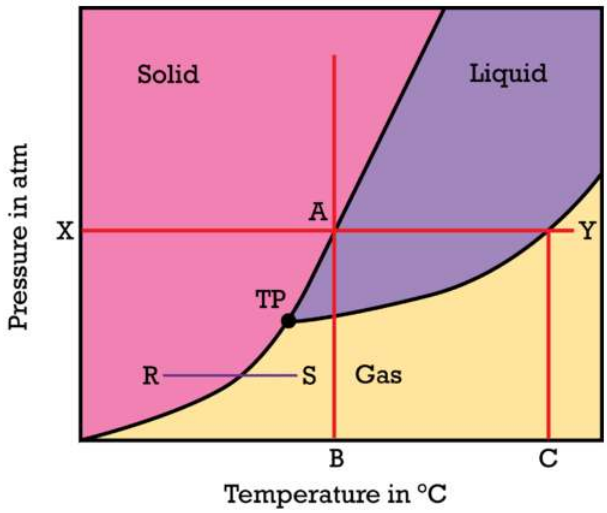



Figure 8.6.1: General phase diagram, which shows the state (phase) of a substance as a function of its temperature and pressure.

Find the $X$ on the pressure axis and presume that the value of $X$ is standard pressure of $1\ \text{atm}$. As one moves left to right across the red line, the temperature of the solid substance is being increased while the pressure remains constant. When point $A$ is reached, the substance melts and the temperature $B$ on the horizontal axis represents the normal melting point of the substance. Moving further to the right, the substance boils at point $Y$ and so point $C$ on the horizontal axis represents the normal boiling point of the substance. As the temperature increases at a constant pressure, the substance changes from solid to liquid to gas.

Start right above point $B$ on the temperature axis and follow the red line vertically. At very low pressure, the particles of the substance are far apart from one another and the substance is in the gas state. As the pressure is increased, the particles of the substance are forced closer and closer together. Eventually the particles are pushed so close together that attractive forces cause the substance to condense into the liquid state. Continually increasing the pressure on the liquid will eventually cause the substance to solidify. For the majority of substances, the solid state is denser than the liquid state and so putting a liquid under great pressure will cause it to turn into a solid. The line segment $R$-$S$ represents the process of sublimation, where the substance changes directly from a solid to a gas. At a sufficiently low pressure, the liquid phase does not exist. The point labeled $TP$ is called the **triple point**. The triple point is the one condition of temperature and pressure where the solid, liquid, and vapor states of a substance can all coexist at equilibrium.

## Phase Diagram for Water

Water is a unique substance in many ways. One of these special properties is the fact that solid water (ice) is less dense than liquid water just above the freezing point. The phase diagram for water is shown in the figure below.

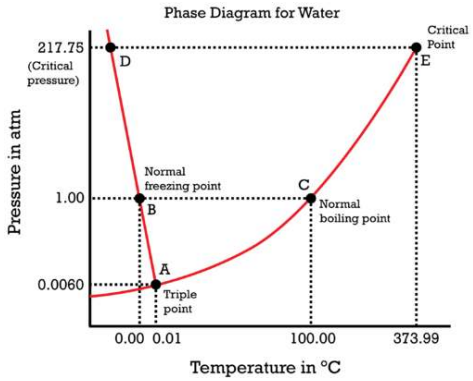



Figure **8.6.1**: Phase diagram for water.

Notice one key difference between last section's general phase diagram, and the above phase diagram for water: in water's diagram, the slope of the line between the solid and liquid states is negative rather than positive. The reason is that water is an unusual substance, in that its solid state is less dense than the liquid state. Ice floats in liquid water. Therefore, a pressure change has the opposite effect on those two phases. If ice is relatively near its melting point, it can be changed into liquid water by the application of pressure. The water molecules are actually closer together in the liquid phase than they are in the solid phase.

Refer again to water's phase diagram (figure above). Notice point ***E***, labeled the **critical point**. What does that mean? At **373.99°C**, particles of water in the gas phase are moving very, very rapidly. At any temperature higher than that, the gas phase cannot be made to liquefy, no matter how much pressure is applied to the gas. The **critical pressure** ($P_C$) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid. For water, the critical pressure is very high, **217.75 atm**. The critical point is the intersection point of the **critical temperature** and the critical pressure.

## Summary

- A phase diagram graphs the conditions of temperature and pressure under which a substance exists in the solid, liquid, and gas states.
- The triple point is the one condition of temperature and pressure where the solid, liquid, and vapor states of a substance can all coexist at equilibrium.

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# 8.7: INTERMOLECULAR FORCES- DISPERSION, DIPOLE–DIPOLE, HYDROGEN BONDING, AND ION-DIPOLE

## LEARNING OBJECTIVES

- To describe the intermolecular forces in liquids.
- Identify the intermolecular forces present in a compound.
- Use intermolecular forces to compare the physical properties of pure compounds.

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 **8.7.1*a***.

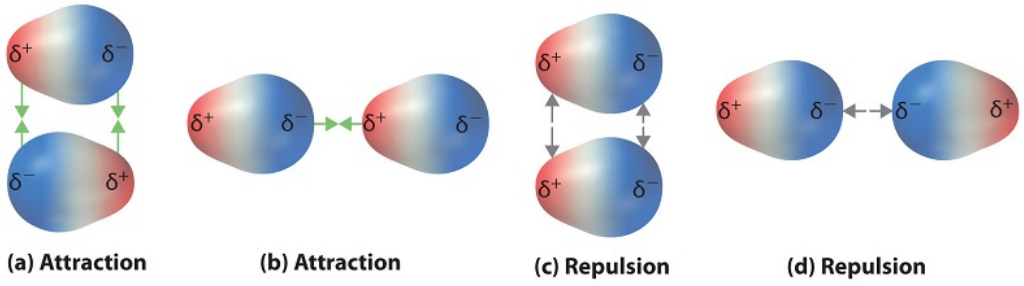



Figure **8.7.1**: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole ($\delta^+$) is near the negative end of another ($\delta^-$) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose 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 **8.7.1*c***). Hence dipole–dipole interactions, such as those in Figure **8.7.1*b***, are *attractive intermolecular interactions*, whereas those in Figure **8.7.1*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 **8.7.2**. On average, however, the attractive interactions dominate.

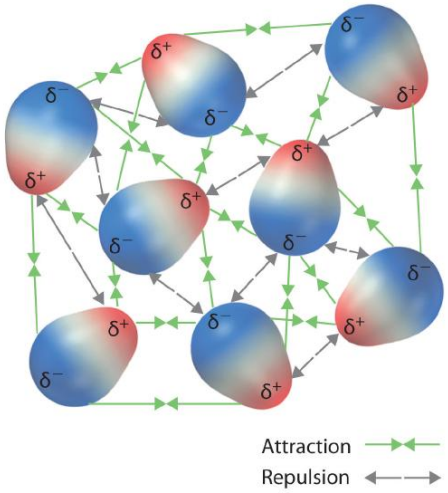



Figure **8.7.2**: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

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 **8.7.1**.

Table **8.7.1**: 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 |

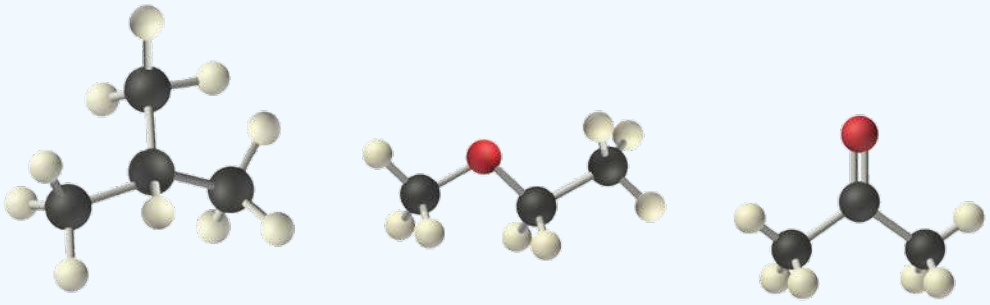
> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*



Video Discussing Dipole Intermolecular Forces. Source: https://youtu.be/ACq_95SIBck

## EXAMPLE 8.7.1

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 8.7.1

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 **8.7.2**).

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 **8.7.2**: 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 **8.7.3**, 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.

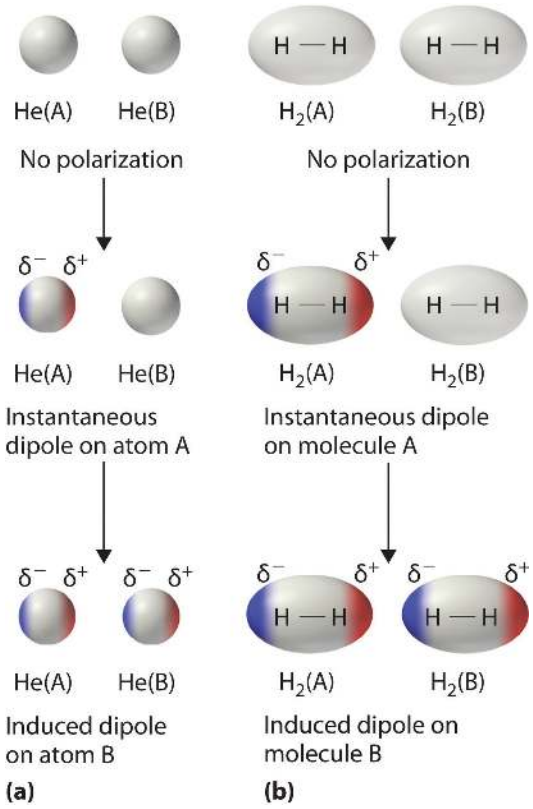



Figure **8.7.3**: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an $H_2$ molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

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 **8.7.3**, tends to become more pronounced as atomic and molecular masses increase (Table **8.7.2**). 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 **8.7.4**). 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 **8.7.4** 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).

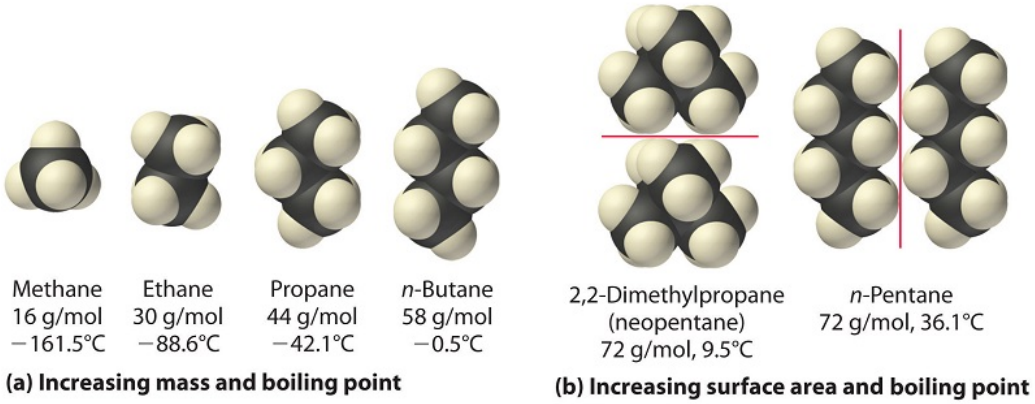



Figure **8.7.4**: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a 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: https://youtu.be/RCRTcIEQ-Hk

## EXAMPLE 8.7.2

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 8.7.2**

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 **8.7.5**. 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.

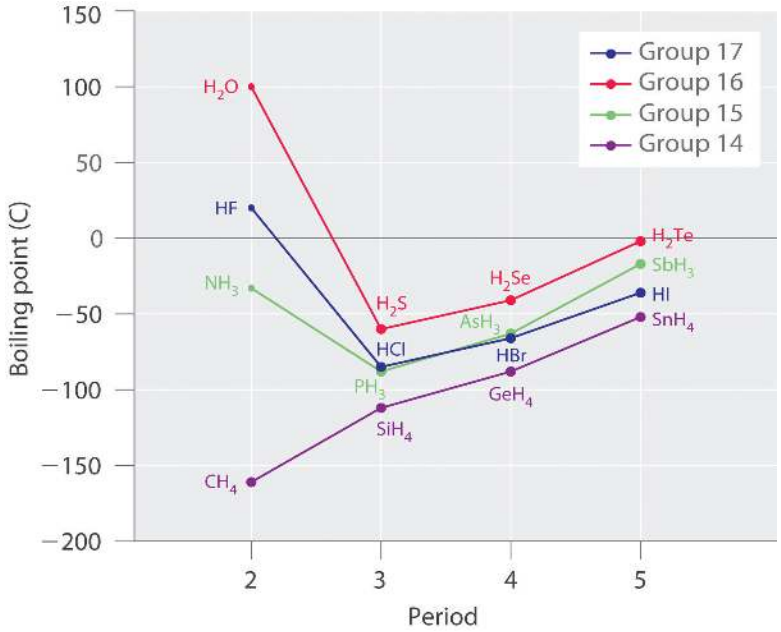



Figure **8.7.5**: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, $NH_3$, and $H_2O$) are anomalously 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. 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 **8.7.6**. 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.

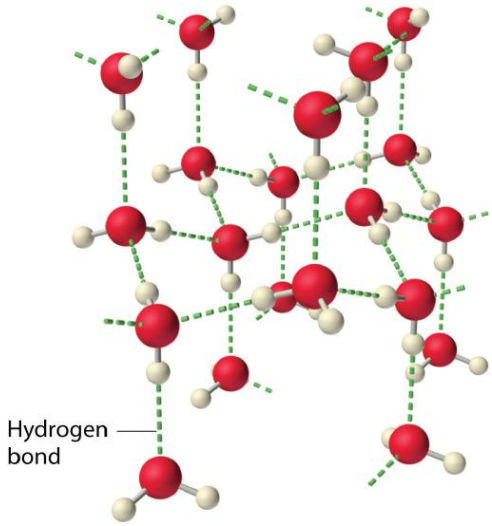



Figure **8.7.6**: The Hydrogen-Bonded Structure of Ice

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.*

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: https://youtu.be/92rbjSpHbr0

### ✔ EXAMPLE 8.7.3

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:**

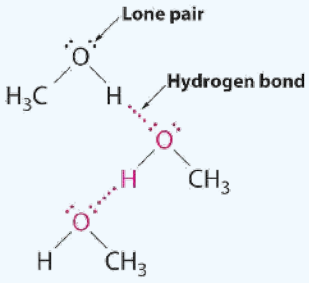
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

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:



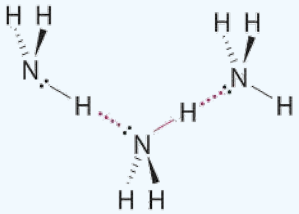

Hydrogen bonding in methanol

## ? EXERCISE 8.7.3

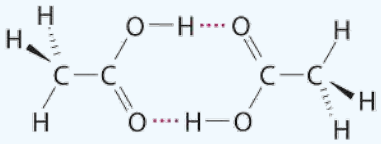
Considering $CH_3CO_2H$, $(CH_3)_3N$, $NH_3$, and $CH_3F$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

**Answer**

$CH_3CO_2H$ and $NH_3$;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

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 8.7.4: 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 8.7.4

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 8.7.5

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 8.7.6

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, cagelike structure that is less dense than liquid water.

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8.7: Intermolecular Forces- Dispersion, Dipole–Dipole, Hydrogen Bonding, and Ion-Dipole is shared under a CC BY-NC-SA 3.0 license and was authored, remixed, and/or curated by LibreTexts.

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# 8.8: Vapor Pressure

**Learning Objectives**

- To describe vapor pressure.
- Use intermolecular forces to compare the vapor pressure of pure liquids.

### What causes this toy to move?

The drinking duck is a toy that many kids (and adults) enjoy playing with. You can see the drinking duck in action in the video below:



The motion of the duck illustrates a physical principle called vapor pressure. As the vapor pressure changes, the liquid in the duck moves up and down, causing the duck to move.

## Vapor Pressure

When a partially filled container of liquid is sealed with a stopper, some liquid molecules at the surface evaporate into the **vapor phase**. However, the vapor molecules cannot escape from the container. So, after a certain amount of time, the space above the liquid reaches a point where it cannot hold any more vapor molecules. Now, some of the vapor molecules condense back into a liquid. The system reaches the point where the rate of evaporation is equal to the rate of condensation (see figure below). This is considered a dynamic equilibrium between the liquid and vapor phase.

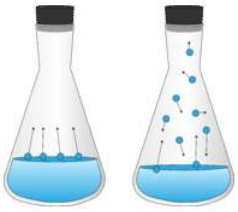


Figure 8.8.1: Equilibrium between liquid phase and vapor phase. (Credit: Christopher Auyeung; Source: CK-12 Foundation; License: CC BY-NC 3.0)

A dynamic equilibrium can be illustrated by an equation with a double arrow, meaning that the reaction is occurring in both directions and at the same rate.

$$\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H_2O}\,(g)$$

The forward direction represents the evaporation process, while the reverse direction represents the condensation process.

Because they cannot escape the container, the vapor molecules above the surface of the liquid exert a pressure on the walls of the container. The **vapor pressure** is a measure of the pressure (force per unit area) exerted by a gas above a liquid in a sealed container. Vapor pressure is a property of a liquid based on the strength of its intermolecular forces. A liquid with weak intermolecular forces evaporates more easily and has a higher vapor pressure. A liquid with stronger intermolecular forces does not evaporate easily, and thus has a lower vapor pressure. For example, diethyl ether is a nonpolar liquid with weak dispersion forces. Its vapor pressure at $20°C$ is $58.96\ kPa$. Water is a polar liquid whose molecules are attracted to one another by relatively strong hydrogen bonding. The vapor pressure of water at $20°C$ is only $2.33\ kPa$, far less than that of diethyl ether.

## Vapor Pressure and Temperature

Vapor pressure is dependent upon temperature. When the liquid in a closed container is heated, more molecules escape the **liquid phase** and evaporate. The greater number of vapor molecules strike the container walls more frequently, resulting in an increase in pressure. The table below shows the temperature dependence of the vapor pressure of three liquids.

**Table 8.8.1: Vapor Pressure (in kPa of Three Liquids at Different Temperatures**

| | 0°C | 20°C | 40°C | 60°C | 80°C | 100°C |
|---|---|---|---|---|---|---|
| Water | 0.61 | 2.33 | 7.37 | 19.92 | 47.34 | 101.33 |
| Ethanol | 1.63 | 5.85 | 18.04 | 47.02 | 108.34 | 225.75 |
| Diethyl Ether | 24.70 | 58.96 | 122.80 | 230.65 | 399.11 | 647.87 |

Notice that the temperature dependence of the vapor pressure is not linear. From $0°C$ to $80°C$, the vapor pressure of water increases by $46.73\ kPa$, while it increases by $53.99\ kPa$ in only a span of twenty degrees from $80°C$ to $100°C$.





## Summary

- Vapor pressure is a measure of the pressure exerted by a gas above a liquid in a sealed container.
- Strong intermolecular forces produce a lower rate of evaporation and a lower vapor pressure.
- Weak intermolecular forces produce a higher rate of evaporation and a higher vapor pressure.
- As the temperature increases, the vapor pressure increases.

## Review

1. Define vapor pressure.
2. How do intermolecular forces affect vapor pressure?
3. How does temperature affect vapor pressure?

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# CHAPTER OVERVIEW

## 9: Solutions and Aqueous Mixtures


9.1: Mixtures
9.2: Solutions - Homogeneous Mixtures
9.3: Solutions of Gases in Water
9.4: Aqueous Solutions - Dissolving solids in water
9.5: Solution Concentration
9.6: Solution Concentration- Molarity
9.7: Solution Dilution
9.8: Properties of Solutions
9.9: Osmosis



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# 9.1: Mixtures

**Learning Objectives**

- Describe and identify different types of mixtures.



Figure 9.1.1 (Credit: JillWellington; Source: https://pixabay.com/photos/lemonade-lemons-poolside-drink-3571083/; License: Pixabay License)

Ahhhh! A tall glass of ice-cold lemonade is really refreshing on a hot day. Lemonade is a combination of lemon juice, water, and sugar. Do you know what kind of matter lemonade is? It's obviously not an element because it consists of more than one substance. Is it a compound? Not all combined substances are compounds. Some—including lemonade—are mixtures.

## What Is a Mixture?

A **mixture** is a combination of two or more substances in any proportion. This is different from a compound, which consists of substances in fixed proportions. The substances in a mixture also do not combine chemically to form a new substance, as they do in a compound. Instead, they just intermingle and keep their original properties. The lemonade pictured above is a mixture because it doesn't have fixed proportions of ingredients. It could have more or less lemon juice, for example, or more or less sugar, and it would still be lemonade.

**Q:** What are some other examples of mixtures?

**A:** Other examples of liquid mixtures include salt water and salad dressing. Air is a mixture of gases, mainly nitrogen and oxygen. The rock pictured in the figure below is a solid mixture.

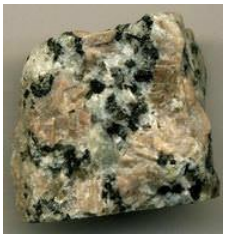


Figure 9.1.2: This rock is a mixture of smaller rocks and minerals. (Credit: James St. John (Flickr: jsj1771); Source: http://www.flickr.com/photos/jsjgeology/8475805063/; License: CC BY 2.0)

## Homogenous Mixtures

A **homogeneous** mixture is a mixture in which the composition is uniform throughout the mixture. The salt water described above is homogeneous because the dissolved salt is evenly distributed throughout the entire salt water sample. Often it is easy to confuse a homogeneous mixture with a pure substance because they are both uniform. The difference is that the composition of the substance is always the same. The amount of salt in the salt water can vary from one sample to another. All solutions would be considered homogeneous because the dissolved material is present in the same amount throughout the solution.

One characteristic of mixtures is that they can be separated into their components. Since each part of the mixture has not reacted with another part of the mixture, the identities of the different materials are unchanged.

## Heterogeneous Mixtures

A **heterogeneous mixture** is a mixture in which the composition is not uniform throughout the mixture. Vegetable soup is a heterogeneous mixture. Any given spoonful of soup will contain varying amounts of the different vegetables and other components of the soup.

A **phase** is any part of a sample that has a uniform composition and properties. By definition, a pure substance or a homogeneous mixture consists of a single phase. A heterogeneous mixture consists of two or more phases. When oil and water are combined, they do not mix evenly, but instead form two separate layers. Each of the layers is called a phase.



Figure **9.1.1**: *Oil and water do not mix, instead forming two distinct layers called phases. The oil phase is less dense than the water phase, and so the oil floats on top of the water.* (Credit: Flickr: Yortw; Source: http://www.flickr.com/photos/yortw/5470226807/; License: CC BY 2.0)

In the case of vegetable soup, one phase would be the liquid soup itself. This phase has vitamins, minerals, and other components dissolved in the water. This phase would be homogeneous. The carrots, peas, corn, or other vegetables represent other phases of the soup.The various vegetables are not mixed evenly in the soup, but are spread around at random.

There are a large number of heterogeneous mixtures around us. Soil is composed of a variety of substances, and is often of different composition depending on the sample taken. One shovelful may come up with dirt and grass, while the next shovelful could contain an earthworm.

Smog is another example of a heterogeneous mixture. This murky collection of pollutants can be a mixture of water and contaminants from burning gasoline or plastics, mixed with nitric oxide derivatives and ozone. You can see that the smog distribution in the air illustrated below is not evenly spread out, but varies from one part of the atmosphere to another.



Figure **9.1.2**: *Smog in New York City.* (Credit: Courtesy of Dr. Edwin P. Ewing, Jr./CDC; Source: http://commons.wikimedia.org/wiki/File:SmogNY.jpg; License: Public Domain)



| Type of Mixture | Description |
|---|---|
| Solutions<br>  <br><br>Figure **9.1.3** (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license) | A **solution** is a homogeneous mixture with tiny particles. The particles are too small to see and also too small to settle or be filtered out of the mixture.<br>When the salt is thoroughly mixed into the water in this glass, it will form a solution. The salt will no longer be visible in the water, and it won't settle to the bottom of the glass. |
| Colloids<br>  <br>Figure **9.1.4** (Credit: Ray Bouknight; Source: http://www.flickr.com/photos/raybouk/9413974806/; License: CC BY 2.0) | A **colloid** is a homogeneous mixture with medium-sized particles. The particles are large enough to see but not large enough to settle or be filtered out of the mixture.<br>The gelatin in this dish is a colloid. It looks red because you can see the red gelatin particles in the mixture. However, the particles are too small to settle to the bottom of the dish. |
| Suspensions<br>  <br>Figure **9.1.5** (Credit: jlarbig; Source: https://pixabay.com/photos/food-dressing-salad-645670/; License: Pixabay License) | A **suspension** is a heterogeneous mixture with large particles. The particles are large enough to see and also to settle or be filtered out of the mixture.<br>The salad dressing in this bottle is a suspension. It contains oil, vinegar, herbs, and spices. If the bottle sits undisturbed for very long, the mixture will separate into its component parts. That's why you should shake it before you use it. |

**Q:** If you buy a can of paint at a paint store, a store employee may put the can on a shaker machine to mix up the paint in the can. What type of mixture is the paint?

**A:** The paint is a suspension. Some of the components of the paint settle out of the mixture when it sits undisturbed for a long time. This explains why you need to shake (or stir) the paint before you use it.

**Q:** The milk you buy in the supermarket has gone through a process called homogenization. This process breaks up the cream in the milk into smaller particles. As a result, the cream doesn't separate out of the milk no matter how long it sits on the shelf. Which type of mixture is homogenized milk?

**A:** Homogenized milk is a colloid. The particles in the milk are large enough to see—that's why milk is white instead of clear like water, which is the main component of milk. However, the particles are not large enough to settle out of the mixture.

## Separating Mixtures

The components of a mixture keep their own identity when they combine, so they retain their physical properties. Examples of physical properties include boiling point, ability to dissolve, and particle size. When components of mixtures vary in physical properties such as these, processes such as boiling, dissolving, or filtering can be used to separate them.

Look at the figure below of the Great Salt Lake in Utah. The water in the lake is a solution of salt and water. Do you see the white salt deposits near the shore? How did the salt separate from the salt water? Water has a lower boiling point than salt, and it evaporates in the heat of the sun. With its higher boiling point, the salt doesn't get hot enough to evaporate, so it is left behind.



Figure 9.1.6: "Great Salt Lake" (Credit: John Morgan; Source: https://www.flickr.com/photos/24742305@N00/3941986636; License: CC BY 2.0)

**Q:** Suppose you have a mixture of salt and pepper. What properties of the salt and pepper might allow you to separate them?

**A:** Salt dissolves in water but pepper does not. If you mix salt and pepper with water, only the salt will dissolve, leaving the pepper floating in the water. You can separate the pepper from the water by pouring the mixture through a filter, such as a coffee filter.

**Q:** After you separate the pepper from the salt water, how could you separate the salt from the water?

**A:** You could heat the water until it boils and evaporates. The salt would be left behind.

## Summary

- A mixture is a combination of two or more substances in any proportions. The substances in a mixture do not combine chemically, so they retain their physical properties.
- A homogeneous mixture has the same composition throughout. A heterogeneous mixture varies in its composition.
- Mixtures can be classified on the basis of particle size into three different types: solutions, suspensions, and colloids.
- The components of a mixture retain their own physical properties. These properties can be used to separate the components by filtering, boiling, or other physical processes.

## Review

1. What is a mixture?
2. What is the difference between a homogeneous and a heterogeneous mixture?
3. Make a table to compare and contrast solutions, colloids, and suspensions. Include an example of each type of mixture in your table.

4. Iron filings are attracted by a magnet. This is a physical property of iron but not of most other materials, including sand. How could you use this difference in physical properties to separate a mixture of iron filings and sand?

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# 9.2: SOLUTIONS - HOMOGENEOUS MIXTURES

## LEARNING OBJECTIVES

- Learn terminology involving solutions.
- Predict if two liquids will make a solution
- Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent.** The minor component of a solution is called the **solute**. By major and minor we mean whichever component has the greater or lesser presence by mass or by moles. Sometimes this becomes confusing, especially with substances with very different molar masses. However, here we will confine the discussion to solutions for which the major component and the minor component are obvious.



Figure **9.2.1**: Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid $\mathbf{NaCl}$ in liquid water, while air is a solution of a gaseous solute ($\mathbf{O_2}$) in a gaseous solvent ($\mathbf{N_2}$). In all cases, however, the overall phase of the solution is the same phase as the solvent. Table **9.2.1** lists some common types of solutions, with examples of each.

Table **9.2.1**: Types of Solutions

| Solvent Phase | Solute Phase | Example |
|---|---|---|
| gas | gas | air |
| liquid | gas | carbonated beverages |
| liquid | liquid | ethanol ($C_2H_5OH$) in $H_2O$ (alcoholic beverages) |
| liquid | solid | salt water |
| solid | gas | $H_2$ gas absorbed by Pd metal |
| solid | liquid | Hg(ℓ) in dental fillings |
| solid | solid | steel alloys |

## EXAMPLE 9.2.1: SUGAR AND WATER

A solution is made by dissolving 1.00 g of sucrose ($\mathbf{C_{12}H_{22}O_{11}}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

### Solution

Either by mass or by moles, the obvious minor component is **sucrose**, so it is **the solute**. **Water**—the majority component—is **the solvent**. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

## EXERCISE 9.2.1

A solution is made by dissolving 3.33 g of $\mathbf{HCl(g)}$ in 40.0 g of liquid methyl alcohol ($\mathbf{CH_3OH}$). Identify the solvent and solute in the resulting solution.

**Answer**

solute: $\mathbf{HCl(g)}$

solvent: $CH_3OH$

## LIQUID - LIQUID SOLUTIONS

A simple way to predict if two liquids will form a solution is to use the phrase "like dissolves like". What this means is that polar compounds dissolve polar compounds, nonpolar compounds dissolve nonpolar compounds, but polar and nonpolar do not dissolve in each other.

Even some nonpolar substances dissolve in water but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, a nonpolar molecule, does dissolve in water—it is this oxygen that the fish take in through their gills. The reason we can enjoy carbonated sodas is also due to a nonpolar compound that dissolves in water. Pepsi-cola and all the other sodas have carbon dioxide gas, $CO_2$, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure.

This general trend of "like dissolves like" is summarized in the following table:

Table 9.2.2: Summary of Solubilities

| Solute (Polarity of Compound) | Solvent (Polarity of Compound) | Dominant Intermolecular Force | Is Solution Formed? |
|---|---|---|---|
| Polar | Polar | Dipole-Dipole Force and/or Hydrogen Bond | yes |
| Non-polar | Non-polar | Dispersion Force | yes |
| Polar | Non-polar | | no |
| Non-polar | Polar | | no |
| Ionic | Polar | Ion-Dipole | yes |
| Ionic | Non-polar | | no |

Note that every time charged particles (ionic compounds or polar substances) are mixed, a solution is formed. When particles with no charges (nonpolar compounds) are mixed, they will form a solution. However, if substances with charges are mixed with other substances without charges, a solution does not form. When an ionic compound is considered "insoluble", it doesn't necessarily mean the compound is completely untouched by water. All ionic compounds dissolve to some extent. An insoluble compound just doesn't dissolve in any noticeable or appreciable amount.

***What is it that makes a solute soluble in some solvents but not others?***

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding. From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane, but not in polar water.



Figure 9.2.2: Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)

### EXAMPLE 9.2.2: POLAR AND NONPOLAR SOLVENTS

Would $I_2$ be more soluble in $CCl_4$ or $H_2O$? Explain your answer.

**Solution**

$I_2$ is nonpolar. Of the two solvents, $CCl_4$ is nonpolar and $H_2O$ is polar, so $I_2$ would be expected to be more soluble in $CCl_4$.

## EXERCISE 9.2.2

Would $C_3H_7OH$ be more soluble in $CCl_4$ or $H_2O$? Explain your answer.

**Answer**

$H_2O$, because both experience hydrogen bonding.

## EXAMPLE 9.2.3

Water is considered a polar solvent. Which substances should dissolve in water?

a. methanol ($CH_3OH$)
b. sodium sulfate (\ce{Na2SO4}\))
c. octane ($C_8H_{18}$)

### Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

a. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
b. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
c. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

## EXERCISE 9.2.3: TOLUENE

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water ($H_2O$)
b. sodium sulfate ($Na_2SO_4$)
c. octane ($C_8H_{18}$)

**Answer**

Octane ($C_8H_{18}$) will dissolve. It is also non-polar.

## SUMMARY

- Solutions are composed of a solvent (major component) and a solute (minor component).
- “Like dissolves like” is a useful rule for deciding if a solute will be soluble in a solvent.

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# 9.3: SOLUTIONS OF GASES IN WATER

## LEARNING OBJECTIVES

- Explain how temperature and pressure affect the solubility of gases.

## GAS SOLUBILITY

The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, $C_6H_{14}$, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure **9.3.1**). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

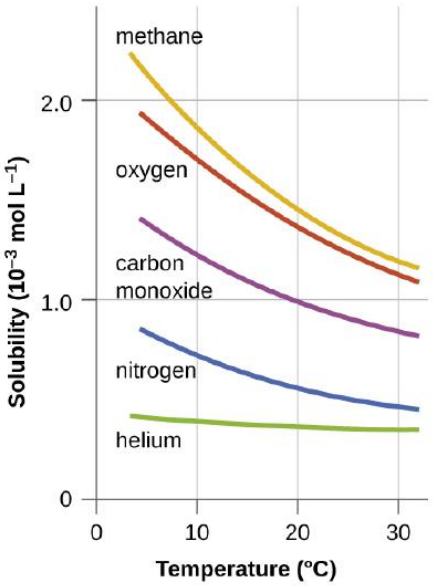



Figure **9.3.1**: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure **9.3.2**).



(a) (b)

Figure **9.3.2**: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (Credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service.)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with $CO_2$ at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure **9.3.3**). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

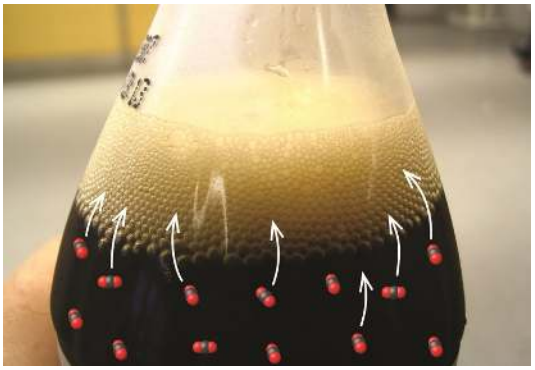


Figure **9.3.3**: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of $CO_2$ is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. A dark brown liquid is shown in a clear, colorless container. A thick layer of beige bubbles appear at the surface of the liquid. In the liquid, thirteen small clusters of single black spheres with two red spheres attached to the left and right are shown. Red spheres represent oxygen atoms and black represent carbon atoms. Seven white arrows point upward in the container from these clusters to the bubble layer at the top of the liquid. (Credit: modification of work by Derrick Coetzee.)

### "FIZZ"

The dissolution in a liquid, also known as fizz, usually involves carbon dioxide under high pressure. When the pressure is reduced, the carbon dioxide is released from the solution as small bubbles, which causes the solution to become effervescent, or fizzy. A common example is the dissolving of carbon dioxide in water, resulting in carbonated water.

Carbon dioxide is weakly soluble in water, therefore it separates into a gas when the pressure is released. This process is generally represented by the following reaction, where a pressurized dilute solution of carbonic acid in water releases gaseous carbon dioxide at decompression:

$$\mathrm{H_2CO_3\,(aq) \longrightarrow H_2O\,(l) + CO_2\,(g)}$$

In simple terms, it is the result of the chemical reaction occurring in the liquid which produces a gaseous product.

For many gaseous solutes, the relation between solubility, $C_g$, and partial pressure, $P_g$, is a proportional one:

$$C_g = kP_g$$

where $k$ is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

## EXAMPLE 9.3.1: APPLICATION OF HENRY'S LAW

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is $1.38 \times 10^{-3}$ mol $L^{-1}$. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

### Solution

According to Henry's law, for an ideal solution the solubility, $C_g$, of a gas ($1.38 \times 10^{-3}$ mol $L^{-1}$, in this case) is directly proportional to the pressure, $P_g$, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both $C_g$ and $P_g$, we can rearrange this expression to solve for $k$.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \\ &\quad (1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1}) \end{aligned}$$

Now we can use $k$ to find the solubility at the lower pressure.

$$C_g = kP_g$$

$$\begin{aligned} &1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ &(\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr}) \\ &= 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

## EXERCISE 9.3.1

A 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of $1.45 \times 10^{-3}$ g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

**Answer**

$7.25 \times 10^{-3}$ g

## CASE STUDY: DECOMPRESSION SICKNESS ("THE BENDS")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventative measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 9.3.4).

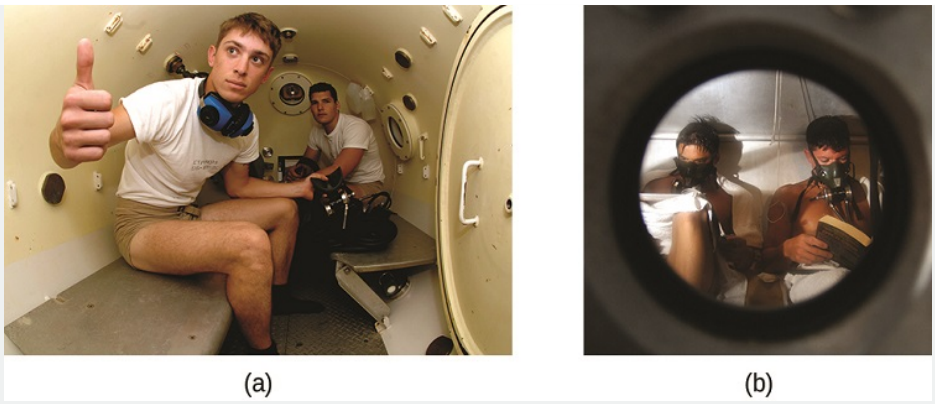
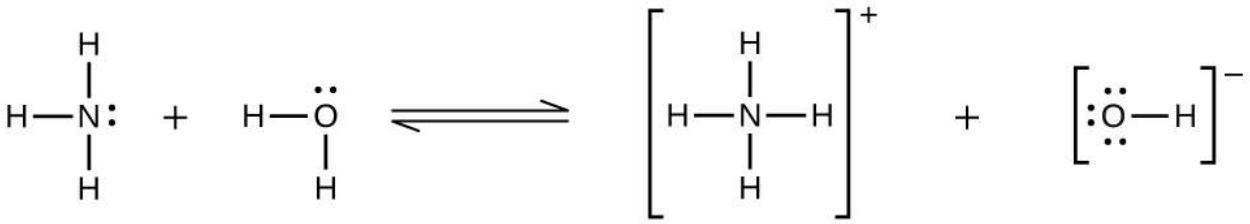



Figure **9.3.4**: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy. Two photos are shown. The first shows two people seated in a steel chamber on benches that run length of the chamber on each side. The chamber has a couple of small circular windows and an open hatch-type door. One of the two people is giving a thumbs up gesture. The second image provides a view through a small, circular window. Inside the two people can be seen with masks over their mouths and noses. The people appear to be reading.

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



This reaction diagram shows three H atoms bonded to an N atom above, below, and two the left of the N. A single pair of dots is present on the right side of the N. This is followed by a plus, then two H atoms bonded to an O atom to the left and below the O. Two pairs of dots are present on the O, one above and the other to the right of the O. A double arrow, with a top arrow pointing right and a bottom arrow pointing left follows. To the right of the double arrow, four H atoms are shown bonded to a central N atom. These 5 atoms are enclosed in brackets with a superscript plus outside. A plus follows, then an O atom linked by a bond to an H atom on its right. The O atom has pairs of dots above, to the left, and below the atom. The linked O and H are enclosed in brackets with superscript minus outside.

Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated.

## CONTRIBUTIONS & ATTRIBUTIONS

- Wikipedia
- 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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# 9.4: Aqueous Solutions - Dissolving solids in water

**Learning Outcomes**

- Define a solution and describe the parts of a solution.
- Describe how an aqueous solution is formed from both ionic compounds and molecular compounds.
- Recognize that some compounds are insoluble in water.
- Describe the differences among strong electrolytes, weak electrolytes, and nonelectrolytes.

## Forming a Solution

When one substance dissolves into another, a solution is formed. A **solution** *is a homogenous mixture consisting of a solute dissolved into a solvent.* The **solute** *is the substance that is being dissolved*, while the **solvent** *is the dissolving medium*. Solutions can be formed with many different types and forms of solutes and solvents. In this chapter, we will focus on solution where the solvent is water. An **aqueous solution** *is water that contains one or more dissolved substance.* The dissolved substances in an aqueous solution may be solids, gases, or other liquids.

In order to be a true solution, a mixture must be stable. When sugar is fully dissolved into water, it can stand for an indefinite amount of time, and the sugar will not settle out of the solution. Further, if the sugar-water solution is passed through a filter, it will remain with the water. This is because the dissolved particles in a solution are very small, usually less than 1 nm in diameter. Solute particles can be atoms, ions, or molecules, depending on the type of substance that has been dissolved.



Figure 9.4.1: When a colored solution is passed through a filter, the entire solution, both solute and solvent, pass through unchanged.

### The Dissolving Process

Water typically dissolves most ionic compounds and polar molecules. Nonpolar molecules, such as those found in grease or oil, do not dissolve in water. We will first examine the process that occurs when an ionic compound, such as table salt (sodium chloride), dissolves in water.

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar; it has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see figure below).

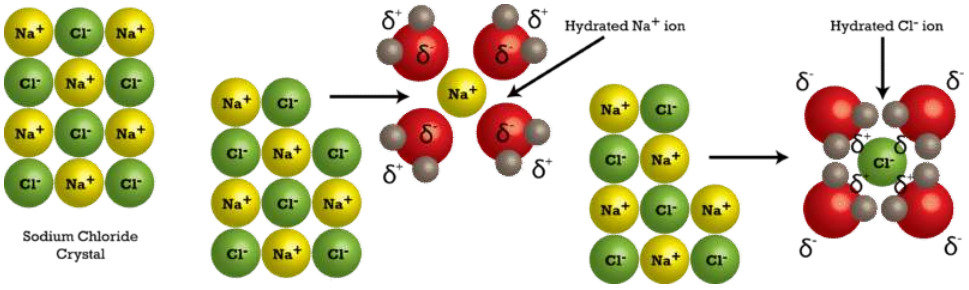



Figure 9.4.2: The process of an ionic sodium chloride crystal being dissolved and hydrated by water.

After coming apart from the crystal, *the individual ions are then surrounded by solvent particles in a process called* **solvation**. Note in the figure above that the individual $Na^+$ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** *is the process of solute particles being surrounded by water molecules arranged in a specific manner*. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is made of the molecular compound sucrose ($C_{12}H_{22}O_{11}$). Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but it *does not break the covalent bonds* between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated. The hydration shell around a molecule of sucrose is arranged so that its partially negative oxygen atoms are near the partially positive hydrogen atoms in the solvent, and vice versa.

### Insoluble Compounds

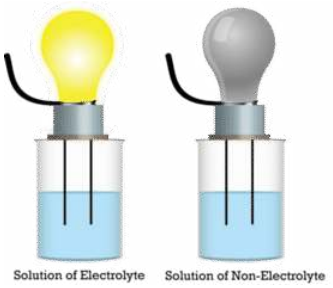
Not all compounds dissolve well in water. Some ionic compounds, such as calcium carbonate ($CaCO_3$) and silver chloride ($AgCl$), are nearly insoluble. This is because the attractions between the ions in the crystal lattice are stronger than the attraction that the water molecules have for the ions. As a result, the crystal remains intact. The solubility of ionic compounds can be predicted using the solubility rules as shown in Table 9.4.1.

***Table* 9.4.1*:*** *Solubility rules for ionic compounds in water.*

| Soluble compounds contain | Except when paired with |
|---|---|
| Group I metal cations or $NH_4^+$ | None |
| $CH_3COO^-$, $NO_3^-$, $ClO_3^-$, or $ClO_4^-$ | None |
| $Cl^-$, $Br^-$, or $I^-$ | $Ag^+$, $Hg_2^{2+}$, $Pb^{2+}$ |
| $SO_4^{2-}$ | $Ag^+$, $Hg_2^{2+}$, $Pb^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ |
| **Insoluble compounds contain** | **Except when paired with** |
| $CO_3^{2-}$, $CrO_4^{2-}$, $PO_4^{3-}$, or $SO_3^{2-}$ | Group I cations or $NH_4^+$ |
| $S^{2-}$ or $OH^-$ | Group I cations or $NH_4^+$, or $Ba^{2+}$ |
| $Ag^+$, $Hg_2^{2+}$, and $Pb^{2+}$ | $CH_3COO^-$, $NO_3^-$, $ClO_3^-$, or $ClO_4^-$ |

## Electrolytes and Nonelectrolytes

An **electrolyte** *is a compound that conducts an electric current when it is dissolved in water or melted.* In order to conduct a current, a substance must contain mobile ions that can move from one electrode to the other. All ionic compounds are electrolytes. When ionic compounds dissolve, they break apart into ions, which are then able to conduct a current. Even insoluble ionic compounds, such as $CaCO_3$, are considered electrolytes because they can conduct a current in the molten (melted) state.




A conductivity apparatus is an incomplete electrical circuit that contains a source of electricity and a light bulb or meter that will show when current is flowing through the circuit. The ends of the incomplete circuit are prongs that can be lowered into a solution. If the prongs are lowered into a solution containing a sufficient number of ions, the circuit will be completed by the solution, current will flow, and the light bulb will light up. If the prongs are lowered into a solution with no ions or an insufficient number of ions, not enough current will flow to light the bulb.

Figure 9.4.4: An apparatus for testing the conductivity of a solution.

A **nonelectrolyte** *is a compound that does not conduct an electric current in either aqueous solution or in the molten state.* Many molecular compounds, such a sugar or ethanol, are nonelectrolytes. When these compounds dissolve in water, they do not produce ions. Illustrated below is the difference between an electrolyte and a nonelectrolyte.

### Dissociation

Earlier, you saw how an ionic crystal lattice breaks apart when it is dissolved in water. **Dissociation** *is the separation of ions that occurs when a solid ionic compound dissolves*. Simply undo the crisscross method that you learned when writing chemical

formulas for ionic compounds, and you are left with the components of an ionic dissociation equation. The subscripts for the ions in the chemical formulas become the coefficients of the respective ions on the product side of the equations. Shown below are dissociation equations for $\mathrm{NaCl}$, $\mathrm{Ca(NO_3)_2}$, and $\mathrm{(NH_4)_3PO_4}$.

$$\mathrm{NaCl}\,(s) \rightarrow \mathrm{Na^+}\,(aq) + \mathrm{Cl^-}\,(aq) \tag{9.4.1}$$
$$\mathrm{Ca(NO_3)_2}\,(s) \rightarrow \mathrm{Ca^{2+}}\,(aq) + 2\mathrm{NO_3^-}\,(aq) \tag{9.4.2}$$
$$\mathrm{(NH_4)_3PO_4}\,(s) \rightarrow 3\mathrm{NH_4^+}\,(aq) + \mathrm{PO_4^{3-}}\,(aq) \tag{9.4.3}$$

One formula unit of sodium chloride dissociates into one sodium ion and one chloride ion. The calcium nitrate formula unit dissociates into one calcium ion and two nitrate ions, because the $2+$ charge of each calcium ion requires two nitrate ions (each with a charge of $1-$) to form an electrically neutral compound. The ammonium phosphate formula unit dissociates into three ammonium ions and one phosphate ion.

Do not confuse the subscripts of the atoms within the polyatomic ion for the subscripts that result from the crisscrossing of the charges that make the original compound neutral. The 3 subscript of the ntirate ion and the 4 subscript of the ammonium ion are part of the polyatomic ion and remain a part of the ionic formula after the compound dissociates. Notice that the compounds are solids $(s)$ that become ions when dissolved in water, producing an aqueous solution $(aq)$.



Figure 9.4.5: Calcium nitrate is a typical ionic compound. In an aqueous solution, it dissociates into calcium ions and nitrate ions.

Nonelectrolytes do not dissociate when forming an aqueous solution. An equation can still be written that simply shows the solid going into solution. For example, the process of dissolving sucrose in water can be written as follows:

$$\mathrm{C_{12}H_{22}O_{11}}\,(s) \rightarrow \mathrm{C_{12}H_{22}O_{11}}\,(aq) \tag{9.4.4}$$

## Strong and Weak Electrolytes

Some polar molecular compounds are nonelectrolytes when the are in their pure state but become electrolytes when they are dissolved in water. Hydrogen chloride $(\mathrm{HCl})$ is a gas in its pure molecular state and is a nonelectrolyte. However, when $\mathrm{HCl}$ is dissolved in water, it conducts a current well because the $\mathrm{HCl}$ molecule ionizes into hydrogen and chloride ions.

$$\mathrm{HCl}\,(g) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{Cl^-}\,(aq) \tag{9.4.5}$$

When $\mathrm{HCl}$ is dissolved into water, it is called hydrochloric acid. Ionic compounds and some polar compounds are completely broken apart into ions and thus conduct a current very well. A **strong electrolyte** *is a solution in which almost all of the dissolved solute exists as ions*.

Some other polar molecular compounds become electrolytes upon being dissolved into water but do not ionize to a very great extent. For example, nitrous acid $(\mathrm{HNO_2})$ only partially ionizes into hydrogen ions and nitrite ions when dissolved in water. Aqueous nitrous acid is composed of only about $5\%$ ions and $95\%$ intact nitrous acid molecules A **weak electrolyte** *is a solution in which only a small fraction of the dissolved solute exists as ions*. The equation showing the ionization of a weak electrolyte utilizes an equilibrium arrow, indicating an equilibrium between the reactants and products.

$$\mathrm{HNO_2}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{NO_2^-}\,(aq) \tag{9.4.6}$$

## Contributors and Attributions

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# 9.5: Solution Concentration

**Learning Objectives**

- Express the amount of solute in a solution in various concentration units.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms with meanings that depend on various factors.

## Introduction

Concentration is the measure of how much of a given substance is mixed with another substance. Solutions are said to be either dilute or concentrated. When we say that vinegar is $5\%$ acetic acid in water, we are giving the concentration. If we said the mixture was $10\%$ acetic acid, this would be more concentrated than the vinegar solution.

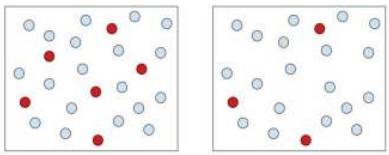


Figure 9.5.1: The solution on the left is more concentrated than the solution on the right because there is a greater ratio of solute (red balls) to solvent (blue balls) particles. The solution particles are closer together. The solution on the right is more dilute (less concentrated). (CC-SA-BY-3.0 Tracy Poulsen).

A **concentrated** solution is one in which there is a large amount of solute in a given amount of solvent. A **dilute** solution is one in which there is a small amount of solute in a given amount of solvent. A dilute solution is a concentrated solution that has been, in essence, watered down. Think of the frozen juice containers you buy in the grocery store. To make juice, you have to mix the frozen juice concentrate from inside these containers with three or four times the container size full of water. Therefore, you are diluting the concentrated juice. In terms of solute and solvent, the concentrated solution has a lot of solute versus the dilute solution that would have a smaller amount of solute.

The terms "concentrated" and "dilute" provide qualitative methods of describing concentration. Although qualitative observations are necessary and have their place in every part of science, including chemistry, we have seen throughout our study of science that there is a definite need for quantitative measurements in science. This is particularly true in solution chemistry. In this section, we will explore some quantitative methods of expressing solution concentration.

There are many ways to express the concentration of a solution. In this section, we will consider mass percent, volume percent, mass-volume percent, and parts per. In the next section, we will look at molarity.

## Mass Percent

There are several ways of expressing the concentration of a solution by using a percentage. The mass/mass percent (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\,\text{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

***mass of solution*** = mass of solute + mass solvent

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Suppose that a solution was prepared by dissolving $25.0\ \text{g}$ of sugar into $100.0\ \text{g}$ of water.

### The mass of the solution is

mass of solution = 25.0g sugar + 100.0g water = 125.0 g

The percent by mass would be calculated by:

$$\text{Percent by mass} = \frac{25.0\text{ g sugar}}{125.0\text{ g solution}} \times 100\% = 20.0\%\text{ sugar}$$

**Example 9.5.1**

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

**Solution**

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\,\text{m/m} = \frac{36.5\text{ g}}{355\text{ g}} \times 100\% = 10.3\%$$

**Exercise 9.5.1**

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of $2.00 \times 10^2$ g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

**Answer**

7.90 %

## Using Mass Percent in Calculations

Sometimes you may want to make up a particular mass of solution of a given percent by mass and need to calculate what mass of the solute to use. Using mass percent as a conversion can be useful in this type of problem. The mass percent can be expressed as a conversion factor in the form $\frac{g\text{ solute}}{100\text{ gsolution}}$ or $\frac{100\text{ gsolution}}{g\text{ solute}}$

For example, if you need to make $3000.0\text{ g}$ of a $5.00\%$ solution of sodium chloride, the mass of solute needs to be determined.

### Solution

**Given:** 3000.0 g NaCl solution

5.00% NaCl solution

**Find:** mass of solute = ? g NaCl

**Other known quantities:** 5.00 g NaCl is to 100 g solution

The appropriate conversion factor (based on the given mass percent) can be used follows:




$$\frac{5.00\ g\ NaCl}{100\ g\ NaCl\ solution}$$

**To solve for the mass of NaCl, the given mass of solution is multiplied by the conversion factor.**

$$g NaCl = 3,000.0\ \cancel{g\ NaCl\ solution} \times \frac{5.00\ g\ NaCl}{100\ \cancel{g\ NaCl\ solution}} = 150.0 g\ NaCl$$

You would need to weigh out $150\text{ g}$ of $\text{NaCl}$ and add it to $2850\text{ g}$ of water. Notice that it was necessary to subtract the mass of the $\text{NaCl}$ $(150\text{ g})$ from the mass of solution $(3000\text{ g})$ to calculate the mass of the water that would need to be added.

**Exercise 9.5.1**

What is the amount (in g) of hydrogen peroxide ($H_2O_2$) needed to make a 6.00 kg, 3.00 % (by mass) $H_2O_2$ solution?

***Answer***

180 g $H_2O_2$

## Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a volume percentage, %vol or (v/v)%:

$$\text{volume percentage} = \dfrac{\text{volume solute}}{\text{volume solution}} \times100\%$$

**Example 9.5.3**: Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

**Solution**

Per the definition of volume percentage, the isopropanol volume is 70% of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

$$\begin{aligned} &355\ \text{mL solution}\left(\frac{70\ \text{mL isopropyl alcohol}}{100\ \text{mL solution}}\right)\left(\frac{0.785\ \text{g isopropyl alcohol}}{1\ \text{mL isopropyl alcohol}}\right) \\ &= 195\ \text{g isopropyl alcohol} \end{aligned}$$

**Exercise 9.5.3**

Wine is approximately 12% ethanol ($CH_3CH_2OH$) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

**Answer**

1.5 mol ethanol

## Mass-Volume Percentage

“Mixed” percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A mass-volume percent is a ratio of a solute’s mass to the solution’s volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as “blood sugar”) is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood (Figure 9.5.2).



(a) (b)

Figure 9.5.2: “Mixed” mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: modification of work by “The National Guard”/Flickr; credit b: modification of work by Biswarup Ganguly).

## Parts per Million and Parts per Billion

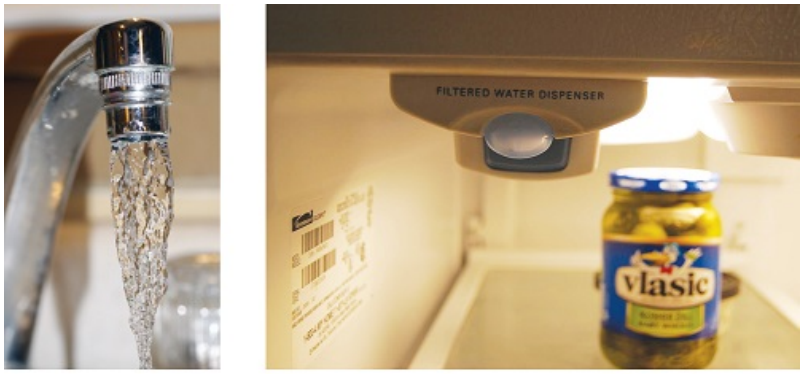
Very low solute concentrations are often expressed using appropriately small units such as parts per million (ppm) or parts per billion (ppb). Like percentage (“part per hundred”) units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm} \tag{9.5.1}$$

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb} \tag{9.5.2}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water (Figure 9.5.3).




(a) (b)

Figure 9.5.3: (a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by “vastateparkstaff”/Wikimedia commons).

### Example 9.5.4: Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

**Solution**

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = $10^3$ ppb). Thus:

$$15 \cancel{\text{ ppb}} \times \frac{1 \text{ ppm}}{10^3 \cancel{\text{ ppb}}} = 0.015 \text{ ppm}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. However, only the volume of solution (300 mL) is given, so we must use the density to derive the corresponding mass. We can assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$$

$$\text{mass solute} = \frac{\text{ppb} \times \text{mass solution}}{10^9 \text{ ppb}}$$

$$\text{mass solute} = \frac{15 \text{ ppb} \times 300 \text{ mL} \times \frac{1.00 \text{ g}}{\text{mL}}}{10^9 \text{ ppb}} = 4.5 \times 10^{-6} \text{ g}$$

Finally, convert this mass to the requested unit of micrograms:

$$4.5 \times 10^{-6} \text{ g} \times \frac{1 \ \mu\text{g}}{10^{-6} \text{ g}} = 4.5 \ \mu\text{g}$$

## Exercise 9.5.4

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

**Answer**

9.6 ppm, 9600 ppb



Measures of Concentration: https://youtu.be/RjMGaUpkg8g

## Summary

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

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# 9.6: Solution Concentration- Molarity

**Learning Objectives**

- Use molarity to determine quantities in chemical reactions.
- Use molarity as a conversion factor in calculations.

## Molarity

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Of all the quantitative measures of concentration, molarity is the one used most frequently by chemists. **Molarity** is defined as the number of moles of solute per liter of solution.

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{9.6.1}$$

The symbol for molarity is $\mathbf{M}$ or moles/liter. Chemists also use square brackets to indicate a reference to the molarity of a substance. For example, the expression $[\mathbf{Ag^+}]$ refers to the molarity of the silver ion in solution. Solution concentrations expressed in molarity are the easiest to perform calculations with, but the most difficult to make in the lab. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

It is important to remember that “mol” in this expression refers to moles of solute and that “L” refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

Sometimes (aq) is added when the solvent is water, as in “3.0 M NaCl (aq).” This is read as "a 3.00 ***molar*** sodium chloride solution," meaning that there are 3.00 moles of NaOH dissolved per one liter of solution.

> *Be sure to note that molarity is calculated as the total volume of the **entire** solution, not just volume of solvent! The solute contributes to total volume.*

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?

Step 1: First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4 \, \cancel{g HCl} \times \frac{1 \, mol \, HCl}{36.5 \, \cancel{g HCl}} = 0.614 \, mol \, HCl$$

Step 2: Now we can use the definition of molarity to determine a concentration:

$$M = \frac{0.614 \, mol \, HCl}{1.56 L \, solution} = 0.394 \, M HCl$$

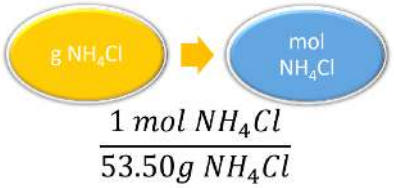
Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters, as demonstrated in the following example.

**Example 9.6.1**

A solution is prepared by dissolving $42.23 \text{ g}$ of $\mathbf{NH_4Cl}$ into enough water to make $500.0 \text{ mL}$ of solution. Calculate its molarity.

**Solution**

Solutions to Example 13.6.1

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>Mass $= 42.23\ \text{g}\ NH_4Cl$<br>Volume solution $= 500.0\ \text{mL} = 0.5000\ \text{L}$<br>Find: Molarity = ? M |
| List other known quantities. | Molar mass $NH_4Cl = 53.50\ \text{g/mol}$ |
| Plan the problem. | 1. The mass of the ammonium chloride is first converted to moles.<br>  <br>$\frac{1\ mol\ NH_4Cl}{53.50g\ NH_4Cl}$<br>2. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters.<br>$\text{M} = \frac{\text{mol}\ NH_4Cl}{\text{L solution}}$ |
| Cancel units and calculate. | Now substitute the known quantities into the equation and solve.<br>$42.23\ \cancel{\text{g}\ NH_4Cl} \times \frac{1\ \text{mol}\ \cancel{NH_4Cl}}{53.50\ \text{g}\ NH_4Cl} = 0.7893\ \text{mol}\ NH_4Cl$<br>$\frac{0.7893\ \text{mol}\ NH_4Cl}{0.5000\ \text{L solution}} = 1.579\ \text{M}$ |
| Think about your result. | The molarity is $1.579\ \text{M}$, meaning that a liter of the solution would contain $1.579\ \text{mol}\ NH_4Cl$. Four significant figures are appropriate. |

**? Exercise 9.6.1*A***

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

**Answer**

1.57 M $C_6H_{12}O_6$

**? Exercise 9.6.1*B***

What is the concentration, in $\text{mol/L}$, where $137\ \text{g}$ of $NaCl$ has been dissolved in enough water to make $500\ \text{mL}$ of solution?

**Answer**

4.69 M NaCl

## Using Molarity in Calculations

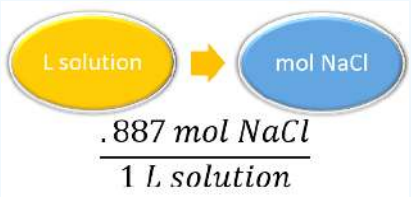
Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition.

### Example 9.6.2: Determining Moles of Solute, Given the Concentration and Volume of a Solution

For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

**Solution**




$$0.108\ \cancel{L\ NaCl} \times \frac{0.887\ mol\ NaCl}{1\ \cancel{L\ solution}} = 0.0958\ mol\ NaCl$$

If we used the definition approach, we get the same answer, but now we are using conversion factor skills.

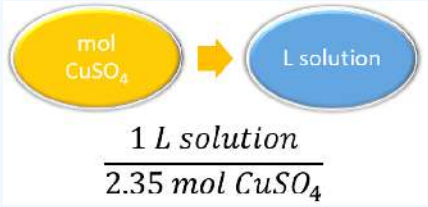
Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

### Example 9.6.3: Determining Volume of a Solution, Given the Concentration and Moles of Solute

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

**Solution**

This is a one-step conversion, but the concentration must be written as the reciprocal for the units to work out:




$$4.88\ \cancel{mol\ CuSO_4} \times \frac{1\ L\ solution}{2.35\ \cancel{mol\ CuSO_4}} = 2.08\ L\ of\ solution$$

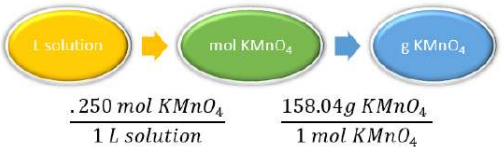
In a laboratory situation, a chemist must frequently prepare a given volume of solutions of a known molarity. The task is to calculate the mass of the solute that is necessary. The molarity equation can be rearranged to solve for moles, which can then be converted to grams. The following example illustrates this.

### Example 9.6.4

A chemist needs to prepare **3.00 L** of a **0.250 M** solution of potassium permanganate (**$KMnO_4$**). What mass of **$KMnO_4$** does she need to make the solution?

**Solution**

Solutions to Example 13.6.4

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>Molarity $= 0.250\ \mathrm{M}$<br>Volume $= 3.00\ \mathrm{L}$<br>Find: Mass $\mathrm{KMnO_4} = ?\ \mathrm{g}$ |
| List other known quantities. | Molar mass $\mathrm{KMnO_4} = 158.04\ \mathrm{g/mol}$<br>0.250 mol $KMnO_4$ to 1 L of $KMnO_4$ solution |
| Plan the problem. |  <br>$\frac{.250\ mol\ KMnO_4}{1\ L\ solution}$ $\frac{158.04g\ KMnO_4}{1\ mol\ KMnO_4}$ |
| Cancel units and calculate. | Now substitute the known quantities into the equation and solve.<br>$\mathrm{mol\ KMnO_4} = 0.250\ \mathrm{M\ KMnO_4} \times 3.00\ \mathrm{L} = 0.750\ \mathrm{mol\ KMnO_4}$<br>$3.00\ \cancel{L\ solution} \times \frac{0.250\ \cancel{\mathrm{mol\ KMnO_4}}}{1\ \cancel{L\ solution}} \times \frac{158.04\ \mathrm{g\ KMnO_4}}{1\ \cancel{\mathrm{mol\ KMnO_4}}} = 119\ \mathrm{g\ KMnO_4}$ |
| Think about your result. | When $119\ \mathrm{g}$ of potassium permanganate is dissolved into water to make $3.00\ \mathrm{L}$ of solution, the molarity is $0.250\ \mathrm{M}$. |

## Exercise 9.6.4A

Using concentration as a conversion factor, how many liters of 0.0444 M $CH_2O$ are needed to obtain 0.0773 mol of $CH_2O$?

**Answer**

1.74 L

## Exercise 9.6.4B

Answer the problems below using concentration as a conversion factor.

a. What mass of solute is present in 1.08 L of 0.0578 M $H_2SO_4$?
b. What volume of 1.50 M HCl solution contains 10.0 g of hydrogen chloride?

**Answer a**

6.12 g

**Answer b**

183 mL or 0.183L

## How to Indicate Concentration

- Square brackets are often used to represent concentration, e.g., [NaOH] = 0.50 M.
- Use the capital letter M for molarity, not a lower case m (this is a different concentration unit called *molality*).




*Watch as the Flinn Scientific Tech Staff demonstrates "How To Prepare Solutions."*

It is important to note that there are many different ways you can set up and solve your chemistry equations. Some students prefer to answer multi-step calculations in one long step, while others prefer to work out each step individually. Neither method is necessarily better or worse than the other method—whichever makes the most sense to ***you*** is the one that you should use. In this text, we will typically use unit analysis (also called dimension analysis or factor analysis).

## Contributors and Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

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# 9.7: SOLUTION DILUTION

**LEARNING OBJECTIVES**

- Explain how concentrations can be changed in the lab.
- Understand how stock solutions are used in the laboratory.

We are often concerned with how much solute is dissolved in a given amount of solution. We will begin our discussion of solution concentration with two related and relative terms: **dilute** and **concentrated**.

- A **dilute** solution is one in which there is a relatively small amount of solute dissolved in the solution.
- A **concentrated** solution contains a relatively large amount of solute.

These two terms do not provide any quantitative information (actual numbers), but they are often useful in comparing solutions in a more general sense. These terms also do not tell us whether or not the solution is saturated or unsaturated, or whether the solution is "strong" or "weak". These last two terms will have special meanings when we discuss acids and bases, so be careful not to confuse them.

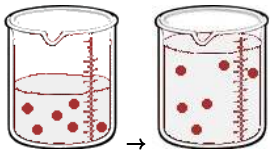
## STOCK SOLUTIONS

It is often necessary to have a solution with a concentration that is very precisely known. Solutions containing a precise mass of solute in a precise volume of solution are called **stock (or standard) solutions.** To prepare a standard solution, a piece of lab equipment called a volumetric flask should be used. These flasks range in size from 10 mL to 2000 mL and are carefully calibrated to a single volume. On the narrow stem is a **calibration mark**. The precise mass of solute is dissolved in a bit of the solvent, and this is added to the flask. Then, enough solvent is added to the flask until the level reaches the calibration mark.

Often, it is convenient to prepare a series of solutions of known concentrations by first preparing a single **stock solution**, as described in the previous section. **Aliquots** (carefully measured volumes) of the stock solution can then be diluted to any desired volume. In other cases, it may be inconvenient to weigh a small mass of sample accurately enough to prepare a small volume of a dilute solution. Each of these situations requires that a solution be diluted to obtain the desired concentration.

## DILUTIONS OF STOCK (OR STANDARD) SOLUTIONS

Imagine we have a salt water solution with a certain concentration. That means we have a certain amount of salt (a certain mass or a certain number of moles) dissolved in a certain volume of solution. Next, we will dilute this solution. This is done by adding more water, not more salt:



**Before Dilution and After Dilution**

The molarity of solution 1 is

$$M_1 = \frac{\text{moles}_1}{\text{liter}_1}$$

and the molarity of solution 2 is

$$M_2 = \frac{\text{moles}_2}{\text{liter}_2}$$

rearrange the equations to find moles:

$$\text{moles}_1 = M_1\text{liter}_1$$

and

$$\text{moles}_2 = M_2\text{liter}_2$$

What stayed the same and what changed between the two solutions? By adding more water, we changed the volume of the solution. Doing so also changed its concentration. **However, the number of moles of solute did not change.** So,

$$moles_1 = moles_2$$

Therefore

$$\boxed{M_1V_1 = M_2V_2} \tag{9.7.1}$$

where

- $M_1$ and $M_2$ are the concentrations of the original and diluted solutions
- $V_1$ and $V_2$ are the volumes of the two solutions

Preparing dilutions is a common activity in the chemistry lab and elsewhere. Once you understand the above relationship, the calculations are simple.

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of $\text{HCl}$. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for $M_2$.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

Another common dilution problem involves calculating what amount of a highly concentrated solution is required to make a desired quantity of solution of lesser concentration. The highly concentrated solution is typically referred to as the stock solution.

### EXAMPLE 9.7.1: DILUTING NITRIC ACID

Nitric acid ($\text{HNO}_3$) is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is $16\ \text{M}$. How much of the stock solution of nitric acid needs to be used to make $8.00\ \text{L}$ of a $0.50\ \text{M}$ solution?

#### Solution

Solutions to Example13.7.1

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>$M_1$, Stock $\text{HNO}_3 = 16\ \text{M}$<br>$V_2 = 8.00\ \text{L}$<br>$M_2 = 0.50\ \text{M}$<br>Find: Volume stock $\text{HNO}_3$ $(V_1) = ?\ \text{L}$ |
| List other known quantities. | none |
| Plan the problem. | First, rearrange the equation algebraically to solve for $V_1$.<br>$V_1 = \frac{M_2 \times V_2}{M_1}$ |
| Calculate and cancel units. | Now substitute the known quantities into the equation and solve.<br>$V_1 = \frac{0.50\ \text{M} \times 8.00\ \text{L}}{16\ \text{M}} = 0.25\ \text{L}$ (9.7.2) |
| Think about your result. | $0.25\ \text{L}$ $(250\ \text{mL})$ of the stock $\text{HNO}_3$ needs to be diluted with water to a final volume of $8.00\ \text{L}$. The dilution is by a factor of 32 to go from $16\ \text{M}$ to $0.5\ \text{M}$. |

### EXERCISE 9.7.1

A 0.885 M solution of KBr with an initial volume of 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

#### Answer

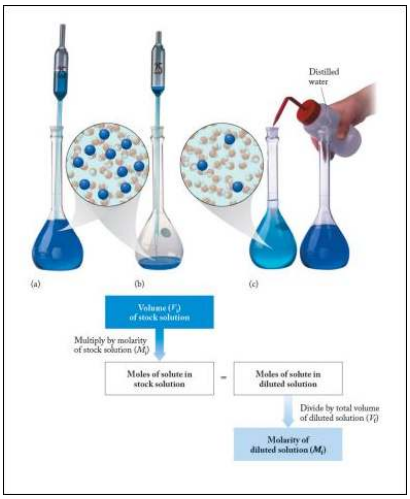
135.4 mL

*Note that the calculated volume will have the same dimensions as the input volume, and dimensional analysis tells us that in this case we don't need to convert to liters, since L cancels when we divide M (mol/L) by M (mol/L).*

Diluting and Mixing Solutions



How to Dilute a Solution by CarolinaBiological




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# 9.8: Properties of Solutions

**Learning Objectives**

- To describe how the properties of solutions differ from those of pure solvents.

Solutions are likely to have properties similar to those of their major component—usually the solvent. However, some solution properties differ significantly from those of the solvent. Here, we will focus on liquid solutions that have a solid solute, but many of the effects we will discuss in this section are applicable to all solutions.

## Colligative Properties

Solutes affect some properties of solutions that depend only on the concentration of the dissolved particles. These properties are called **colligative properties**. Four important colligative properties that we will examine here are vapor pressure depression, boiling point elevation, freezing point depression, and osmotic pressure.

Molecular compounds separate into individual molecules when they are dissolved, so for every 1 mol of molecules dissolved, we get 1 mol of particles. In contrast, ionic compounds separate into their constituent ions when they dissolve, so 1 mol of an ionic compound will produce more than 1 mol of dissolved particles. For example, every mole of NaCl that dissolves yields 1 mol of $Na^+$ ions and 1 mol of $Cl^-$ ions, for a total of 2 mol of particles in solution. Thus, the effect on a solution's properties by dissolving NaCl may be twice as large as the effect of dissolving the same amount of moles of glucose ($C_6H_{12}O_6$).

## Vapor Pressure Depression

All liquids evaporate. In fact, given enough volume, a liquid will turn completely into a vapor. If enough volume is not present, a liquid will evaporate only to the point where the rate of evaporation equals the rate of vapor condensing back into a liquid. The pressure of the vapor at this point is called the **vapor pressure** of the liquid.

The presence of a dissolved solid lowers the characteristic vapor pressure of a liquid so that it evaporates more slowly. (The exceptions to this statement are if the solute itself is a liquid or a gas, in which case the solute will also contribute something to the evaporation process. We will not discuss such solutions here.) This property is called vapor pressure depression and is depicted in Figure **9.8.1**.

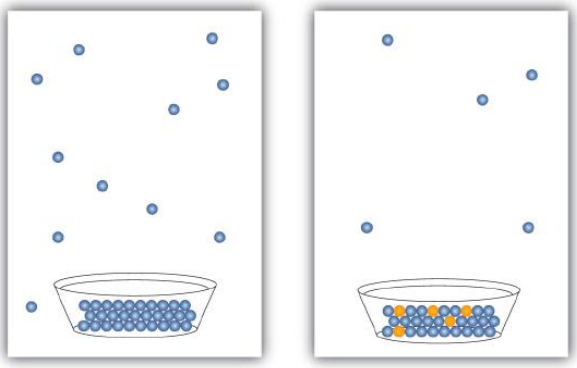


Figure **9.8.1**: Vapor Pressure Depression. The presence of solute particles blocks some of the ability for liquid particles to evaporate. Thus, solutions of solid solutes typically have a lower vapor pressure than the pure solvent.

## Boiling Point Elevation

A related property of solutions is that their boiling points are *higher* than the boiling point of the pure solvent. Because the presence of solute particles decreases the vapor pressure of the liquid solvent, a higher temperature is needed to reach the boiling point. This phenomenon is called boiling point elevation. For every mole of particles dissolved in a liter of water, the boiling point of water increases by about 0.51°C. The addition of one mole of sucrose (molecular compound) in one liter of water will raise the boiling point from 100°C to 100.51°C but the addition of one mole of NaCl in one liter of water will raise the boiling point by 2 x 0.51°C = 1.02°C. Furthermore, the addition of one mole of $CaCl_2$ in one liter of water will raise the boiling point by 3 x 0.51°C = 1.53°C.

Some people argue that putting a pinch or two of salt in water used to cook spaghetti or other pasta makes a solution that has a higher boiling point, so the pasta cooks faster. In actuality, the amount of solute is so small that the boiling point of the water is practically unchanged.

### Freezing Point Depression

The presence of solute particles has the opposite effect on the freezing point of a solution. When a solution freezes, only the solvent particles come together to form a solid phase, and the presence of solute particles interferes with that process. Therefore, for the liquid solvent to freeze, more energy must be removed from the solution, which lowers the temperature. Thus, solutions have lower freezing points than pure solvents do. This phenomenon is called freezing point depression. For every mole of particles in a liter of water, the freezing point decreases by about 1.86°C.

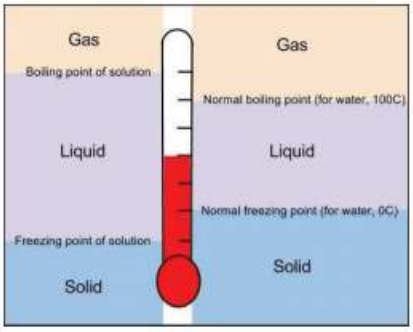



Figure **9.8.2**: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

Both boiling point elevation and freezing point depression have practical uses. For example, solutions of water and ethylene glycol ($C_2H_6O_2$) are used as coolants in automobile engines because the boiling point of such a solution is greater than 100°C, the normal boiling point of water. In winter, salts like NaCl and $CaCl_2$ are sprinkled on the ground to melt ice or keep ice from forming on roads and sidewalks (Figure **9.8.3**). This is because the solution made by dissolving sodium chloride or calcium chloride in water has a lower freezing point than pure water, so the formation of ice is inhibited.



Figure **9.8.3**: Effect of Freezing Point Depression. The salt sprinkled on this sidewalk makes the water on the sidewalk have a lower freezing point than pure water, so it does not freeze as easily. This makes walking on the sidewalk less hazardous in winter. © Thinkstock

## Comparing the Freezing and Boiling Point of Solutions

Recall that covalent and ionic compounds do not dissolve in the same way. Ionic compounds break up into cations and anions when they dissolve. Covalent compounds typically do not break up. For example a sugar/water solution stays as sugar and water, with the sugar molecules staying as molecules. Remember that colligative properties are due to the number of solute particles in the solution. Adding 10 molecules of sugar to a solvent will produce 10 solute particles in the solution. When the solute is ionic, such as $NaCl$ however, adding 10 formulas of solute to the solution will produce 20 ions (solute particles) in the solution. Therefore, adding enough $NaCl$ solute to a solvent to produce a $0.20\ m$ solution will have twice the effect of adding enough sugar to a solvent to produce a $0.20\ m$ solution. Colligative properties depend on the number of solute particles in the solution.

"$i$" is the number of particles that the solute will dissociate into upon mixing with the solvent. For example, sodium chloride, $\mathbf{NaCl}$, will dissociate into two ions so for $\mathbf{NaCl}$, $i = 2$; for lithium nitrate, $\mathbf{LiNO_3}$, $i = 2$; and for calcium chloride, $\mathbf{CaCl_2}$, $i = 3$. For covalent compounds, $i$ is always equal to 1.

By knowing the *molality* of a solution and the number of particles a compound will dissolve to form, it is possible to predict which solution in a group will have the lowest freezing point. To compare the boiling or freezing points of solutions, follow these general steps:

1. Label each solute as ionic or covalent.
2. If the solute is ionic, determine the number of *ions* in the formula. Be careful to look for polyatomic ions.
3. Multiply the original molality ($\mathbf{m}$) of the solution by the number of particles formed when the solution dissolves. This will give you the total concentration of particles dissolved.
4. Compare these values. The higher total concentration will result in a higher boiling point and a lower freezing point.

### ✔ Example 9.8.1

Rank the following solutions in water in order of *increasing* (lowest to highest) freezing point:

- $\mathbf{0.1\ m\ NaCl}$
- $\mathbf{0.1\ m\ C_6H_{12}O_6}$
- $\mathbf{0.1\ m\ CaI_2}$

#### Solution

To compare freezing points, we need to know the total concentration of all particles when the solute has been dissolved.

- $\mathbf{0.1\ m\ NaCl}$: This compound is ionic (metal with nonmetal), and will dissolve into 2 parts. The total final concentration is: $\mathbf{(0.1\ m)\ (2) = 0.2\ m}$
- $\mathbf{0.1\ m\ C_6H_{12}O_6}$: This compound is covalent (nonmetal with nonmetal), and will stay as 1 part. The total final concentration is: $\mathbf{(0.1\ m)\ (1) = 0.1\ m}$
- $\mathbf{0.1\ m\ CaI_2}$: This compound is ionic (metal with nonmetal), and will dissolve into 3 parts. The total final concentration is: $\mathbf{(0.1\ m)\ (3) = 0.3\ m}$

Remember, the greater the concentration of particles, the lower the freezing point will be. $\mathbf{0.1\ m\ CaI_2}$ will have the lowest freezing point, followed by $\mathbf{0.1\ m\ NaCl}$, and the highest of the three solutions will be $\mathbf{0.1\ m\ C_6H_{12}O_6}$, but all three of them will have a lower freezing point than pure water.✔ Example $\mathbf{9.8.1}$

Which solution's freezing point deviates more from that of pure water—a 1 M solution of NaCl or a 1 M solution of $\mathbf{CaCl_2}$?

#### Solution

Colligative properties depend on the number of dissolved particles, so the solution with the greater number of particles in solution will show the greatest deviation. When NaCl dissolves, it separates into two ions, $Na^+$ and $Cl^-$. But when $\mathbf{CaCl_2}$ dissolves, it separates into three ions—one $Ca^{2+}$ ion and two $Cl^-$ ions. Thus, mole for mole, $\mathbf{CaCl_2}$ will have 50% more impact on freezing point depression than NaCl.

### ? Exercise 9.8.1

Which solution's boiling point deviates more from that of pure water—a 1 M solution of $\mathbf{CaCl_2}$ or a 1 M solution of $MgSO_4$?

#### Answer

$\mathbf{CaCl_2}$

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# 9.9: Osmosis

**Learning Objectives**

- Describe osmosis.
- Apply osmosis to the movement of water in and out of the cell.

## Osmosis

Before we introduce the final colligative property, we need to present a new concept. A **semipermeable membrane** is a thin membrane that will pass certain small molecules, but not others. A thin sheet of cellophane, for example, acts as a semipermeable membrane. Consider the system in Figure **9.9.1**.

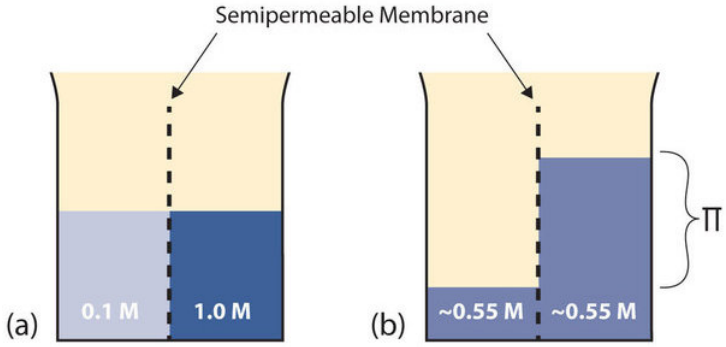



Figure **9.9.1**: Osmosis. (a) Two solutions of differing concentrations are placed on either side of a semipermeable membrane. (b) When osmosis occurs, solvent molecules selectively pass through the membrane from the dilute solution to the concentrated solution, diluting it until the two concentrations are the same. The pressure exerted by the different height of the solution on the right is called the osmotic pressure. (CC BY-SA-NC 3.0; anonymous)

a. A semipermeable membrane separates two solutions having the different concentrations marked. Curiously, this situation is not stable; there is a tendency for water molecules to move from the dilute side (on the left) to the concentrated side (on the right) until the concentrations are equalized, as in Figure **9.9.1***b*.
b. This tendency is called **osmosis**. In osmosis, the solute remains in its original side of the system; only solvent molecules move through the semipermeable membrane. In the end, the two sides of the system will have different volumes. Because a column of liquid exerts a pressure, there is a pressure difference (Π) on the two sides of the system that is proportional to the height of the taller column. This pressure difference is called the **osmotic pressure**, which is a colligative property.

The osmotic pressure of a solution is easy to calculate:

$$\Pi = MRT$$

where Π is the osmotic pressure of a solution, $M$ is the molarity of the solution, $R$ is the ideal gas law constant, and $T$ is the absolute temperature. This equation is reminiscent of the ideal gas law we considered in Chapter 6.

**Example 9.9.5: Osmotic Pressure**

What is the osmotic pressure of a 0.333 M solution of $C_6H_{12}O_6$ at 25°C?

**Solution**

First we need to convert our temperature to kelvins:

$$T = 25 + 273 = 298 \text{ K}$$

Now we can substitute into the equation for osmotic pressure, recalling the value for $R$:

$$\Pi = (0.333M)\left(0.08205\frac{L.atm}{mol.K}\right)(298K)$$

The units may not make sense until we realize that molarity is defined as moles per liter:

$$\Pi = \left(0.333 \frac{mol}{L}\right)\left(0.08205 \frac{L.atm}{mol.K}\right)(298K)$$

Now we see that the moles, liters, and kelvins cancel, leaving atmospheres, which is a unit of pressure. Solving,

$$\Pi = 8.14\,atm$$

This is a substantial pressure! It is the equivalent of a column of water 84 m tall.

**? Exercise 9.9.5**

What is the osmotic pressure of a 0.0522 M solution of $C_{12}H_{22}O_{11}$ at 55°C?

**Answer**

1.40 atm

Osmotic pressure is important in biological systems because cell walls are semipermeable membranes. In particular, when a person is receiving intravenous (IV) fluids, the osmotic pressure of the fluid needs to be approximately the same as blood serum to avoid any negative consequences. Figure **9.9.3** shows three red blood cells:

- A healthy red blood cell.
- A red blood cell that has been exposed to a lower concentration than normal blood serum (a *hypotonic* solution); the cell has plumped up as solvent moves into the cell to dilute the solutes inside.
- A red blood cell exposed to a higher concentration than normal blood serum (*hypertonic*); water leaves the red blood cell, so it collapses onto itself. Only when the solutions inside and outside the cell are the same (*isotonic*) will the red blood cell be able to do its job.

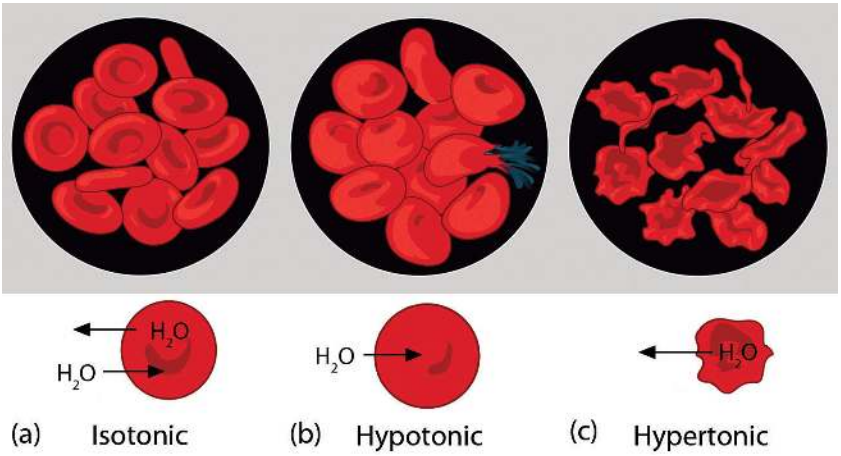



Figure **9.9.3**: Osmotic Pressure and Red Blood Cells. (a) This is what a normal red blood cell looks like. (b) When a red blood cell is exposed to a hypotonic solution, solvent goes through the cell membrane and dilutes the inside of the cell. (c) When a red blood cell is exposed to a hypertonic solution, solvent goes from the cell to the surrounding solution, diluting the hypertonic solution and collapsing the cell. Neither of these last two cases is desirable, so IV solutions must be isotonic with blood serum to not cause deleterious effects. (Public Domain; Mariana Ruiz Villareal)

Osmotic pressure is also the reason you should not drink seawater if you're stranded on a lifeboat in the ocean; seawater has a higher osmotic pressure than most of the fluids in your body. You *can* drink the water, but ingesting it will pull water out of your cells as osmosis works to dilute the seawater. Ironically, your cells will die of thirst, and you will also die. (It is okay to drink the water if you are stranded on a body of freshwater, at least from an osmotic pressure perspective.) Osmotic pressure is also thought to be important—in addition to capillary action—in getting water to the tops of tall trees.

## Summary

- Osmotic pressure is caused by concentration differences between solutions separated by a semipermeable membrane, and is an important biological consideration.

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# CHAPTER OVERVIEW

## 10: Reaction Rates and Equilibrium


10.1: Chemical Reaction Rate

10.2: Collisions Theory and Reaction Rates

10.3: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

10.4: Dynamic Equilibrium

10.5: The Equilibrium Constant Expression

10.6: Le Chatelier's Principle


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# 10.1: Chemical Reaction Rate

**Learning Objectives**

- Define chemical reaction rate
- Calculate reaction rates from experimental data

Drag racing is a sport that involves two cars starting from a dead stop, and driving as fast as they can down a quarter-mile strip. At the end of the strip are timers that determine both elapsed time (how long it took for the cars to cover the quarter mile) and top speed (how fast they were going as they went through the timer chute). Both pieces of data are important. One car may accelerate faster and get ahead that way, while the other car may be slower off the line, but can get up to a higher top speed at the end of the run.

## Chemical Reaction Rate

Chemical reactions vary widely in terms of the speed with which they occur. Some reactions occur very quickly. If a lit match is brought in contact with lighter fluid or another flammable liquid, it erupts into flames instantly and burns fast. Other reactions occur very slowly. A container of milk in the refrigerator will be good to drink for weeks before it begins to turn sour. Millions of years were required for dead plants under Earth's surface to accumulate and eventually turn into fossil fuels such as coal and oil.

Chemists need to be concerned with the rates at which chemical reactions occur. Rate is another word for speed. If a sprinter takes $11.0\ \text{s}$ to run a $100\ \text{m}$ dash, his rate is given by the distance traveled divided by the time.

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100\ \text{m}}{11.0\ \text{s}} = 9.09\ \text{m/s}$$

The sprinter's average running rate for the race is $9.09\ \text{m/s}$. We say that it is his average rate because he did not run at that speed for the entire race. At the very beginning of the race, while coming from a standstill, his rate must be slower until he is able to get up to his top speed. His top speed must then be greater than $9.09\ \text{m/s}$ so that, taken over the entire race, the average ends up at $9.09\ \text{m/s}$.



Figure 10.1.1: Runner. (CC BY-NC; CK-12)

Chemical reactions can't be measured in units of meters per second, as that would not make any sense. A **reaction rate** is the change in concentration of a reactant or product with time. Suppose that a simple reaction were to take place in which a $1.00\ \text{M}$ aqueous solution of substance $\text{A}$ was converted to substance $\text{B}$.

$$\text{A}\,(aq) \rightarrow \text{B}\,(aq)$$

Suppose that after 20.0 seconds, the concentration of $\text{A}$ had dropped from $1.00\ \text{M}$ to $0.72\ \text{M}$ as $\text{A}$ was slowly being converted to $\text{B}$. We can express the rate of this reaction as the change in concentration of $\text{A}$ divided by time.

$$\text{rate} = -\frac{\Delta\,[\text{A}]}{\Delta t} = -\frac{[\text{A}]_{\text{final}} - [\text{A}]_{\text{initial}}}{\Delta t}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of $\text{A}$ is its final concentration minus its initial concentration. Because the concentration of $\text{A}$ is decreasing over time, the negative sign is used. Thus, the rate for the reaction is positive and the units are molarity per second or $\text{M/s}$.

$$\text{rate} = -\frac{0.72\ \text{M} - 1.00\ \text{M}}{20.0\ \text{s}} = -\frac{-0.28\ \text{M}}{20.0\ \text{s}} = 0.014\ \text{M/s}$$

The molarity of A decreases by an average rate of 0.014 M every second. In summary, the rate of a chemical reaction is measured by the change in concentration over time for a reactant or product. The unit of measurement for a reaction rate is molarity per second (M/s).

### Example

If we measure the concentration of hydrogen peroxide, $H_2O_2$, in an aqueous solution, we find that it changes slowly over time as the $H_2O_2$ decomposes, according to the equation:

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned}\text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t}\end{aligned}$$

This mathematical representation of the change in species concentration over time is the rate expression for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[H_2O_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time $t_1$; likewise, $[H_2O_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time $t_2$; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval $\Delta t$ (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. Figure 10.1.1 provides an example of data collected during the decomposition of $H_2O_2$.

| Time (h) | $[H_2O_2]$ (mol $L^{-1}$) | $\Delta[H_2O_2]$ (mol $L^{-1}$) | $\Delta t$ (h) | Rate of Decomposition, (mol/L/h) |
|---|---|---|---|---|
| 0.00 | 1.000 | | | |
| | | −0.500 | 6.00 | −0.0833 |
| 6.00 | 0.500 | | | |
| | | −0.250 | 6.00 | −0.0417 |
| 12.00 | 0.250 | | | |
| | | −0.125 | 6.00 | −0.0208 |
| 18.00 | 0.125 | | | |
| | | −0.062 | 6.00 | −0.0103 |
| 24.00 | 0.0625 | | | |

Figure 10.1.1: The rate of decomposition of $H_2O_2$ in an aqueous solution decreases as the concentration of $H_2O_2$ decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500\text{ mol/L} - 1.000\text{ mol/L})}{(6.00\text{ h} - 0.00\text{ h})} = 0.0833\text{ mol L}^{-1}\text{ h}^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.0625\text{ mol/L} - 0.125\text{ mol/L})}{(24.00\text{ h} - 18.00\text{ h})} = 0.0104\text{ mol L}^{-1}\text{ h}^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an average rate for the reaction over this time interval.

# Summary

- Chemists need to be concerned with the rates at which chemical reactions occur.
- The reaction rate indicates how fast the reaction proceeds.

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# 10.2: Collisions Theory and Reaction Rates

**Learning Objectives**

- Describe collision theory and its connection to reaction rates.
- Define activation energy and how it relates to energy diagrams.
- Use collision theory to describe how concentration, temperature, and catalysts affect reaction rates.

## Collision Theory

**Postulates of Collision theory**

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\#\ \text{collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

The behavior of the reactant atoms, molecules, or ions is responsible for the rates of a given chemical reaction. **Collision theory** *is a set of principles based around the idea that reactant particles form products when they collide with one another, but only when those collisions have enough kinetic energy and the correct orientation to cause a reaction.* Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another, and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other product. The first collision is called an ineffective collision, while the second collision is called an effective collision.

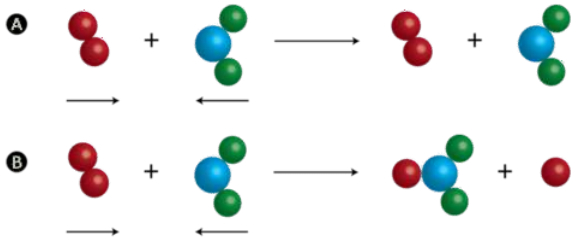



Figure 10.2.1: (A) An ineffective collision is one that does not result in product formation. (B) An effective collision is one in which chemical bonds are broken, and a product is formed.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break and a chemical reaction more likely to occur when those particles collide with other particles. Additionally, more energetic particles have more forceful collisions, which also increases the likelihood that a rearrangement of atoms will take place. The **activation energy** *for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction*. Some reactions occur readily at room temperature because most of the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy to react unless more is provided by an external source of heat.

### Potential Energy Diagrams

Then energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, sometimes called a reaction progress curve. A **potential energy diagram** *shows the change in the potential energy of a system as reactants are converted into products*. The figure below shows basic potential energy diagrams for an endothermic (left) and an exothermic (right) reaction. Recall that the enthalpy change ($\Delta H$) is positive for an endothermic reaction and negative for an

exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

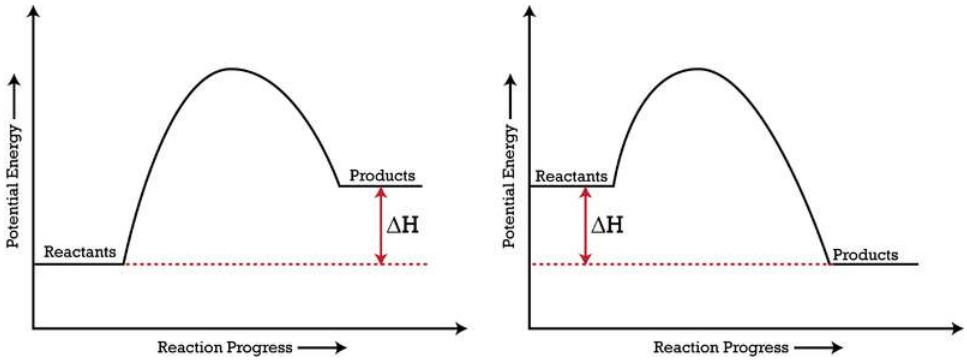



Figure 10.2.2: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (Left) In an endothermic reaction, the energy of the products is greater than the energy of the reactants, and $\Delta H$ is positive. (Right) In an exothermic reaction, the energy of the products is lower than the energy of the reactants, and $\Delta H$ is negative.

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide, they can overcome this barrier (see figure below).

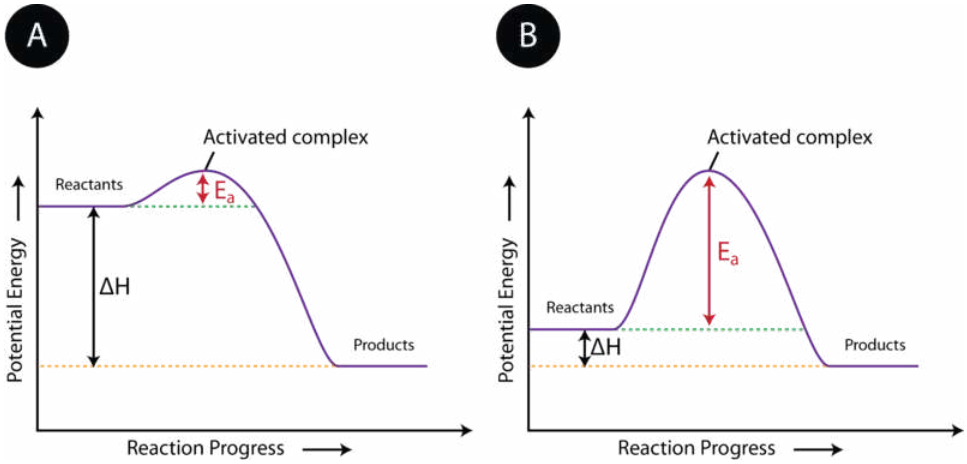



Figure 10.2.3: The activation energy $(E_a)$ of a reaction is the barrier that must be overcome in order for the reactants to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow.

As discussed earlier, reactant particles sometimes collide with one another and yet remain unchanged by the collision. Other times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** *is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier*. Because of its high energy, the activated complex exists only for an extremely short period of time (about $10^{-13}$ s). The activated complex is equally likely to either reform the original reactants or go on to form the products. The figure below shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules. Because of their unstable nature and brief existence, very little is known about the exact structures of most activated complexes.

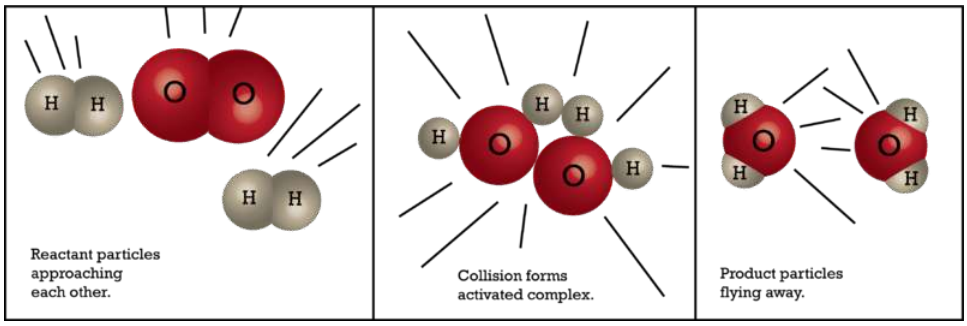



Figure **10.2.4**: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve.

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# 10.3: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

**Learning Outcomes**

- Describe how changing the temperature and concentration of a reaction affects the rate of a reaction.
- Define a catalyst and how a catalyst affects the rate of a reaction.

By their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reaction conditions can have an effect on the rate of a given chemical reaction. Collision theory can be utilized to explain these rate effects.

## Effect of Temperature on Rate of Reaction

The rate of reaction was discussed in terms of three factors: collision frequency, the collision energy, and the geometric orientation. Remember that the collision frequency is the number of collisions per second. The collision frequency is dependent, among other factors, on the temperature of the reaction.

When the temperature is increased, the average velocity of the particles is increased. The average kinetic energy of these particles is also increased. The result is that the particles will collide more frequently, because the particles move around faster and will encounter more reactant particles. However, this is only a minor part of the reason why the rate is increased. Just because the particles are colliding more frequently does not mean that the reaction will definitely occur.

The major effect of increasing the temperature is that more of the particles that collide will have the amount of energy needed to have an effective collision. In other words, more particles will have the necessary activation energy.

At room temperature, the hydrogen and oxygen in the atmosphere do not have sufficient energy to attain the activation energy needed to produce water:

$$\mathrm{O_2}\,(g) + \mathrm{H_2}\,(g) \rightarrow \text{No reaction}$$

At any one moment in the atmosphere, there are many collisions occurring between these two reactants. But what we find is that water is not formed from the oxygen and hydrogen molecules colliding in the atmosphere, because the activation energy barrier is just too high, and all the collisions are resulting in rebound. When we increase the temperature of the reactants or give them energy in some other way, the molecules have the necessary activation energy and are able to react to produce water:

$$\mathrm{O_2}\,(g) + \mathrm{H_2}\,(g) \rightarrow \mathrm{H_2O}\,(l)$$

There are times when the rate of a reaction needs to be slowed down. Lowering the temperature could also be used to decrease the number of collisions that would occur and lowering the temperature would also reduce the kinetic energy available for activation energy. If the particles have insufficient activation energy, the collisions will result in rebound rather than reaction. Using this idea, when the rate of a reaction needs to be lower, keeping the particles from having sufficient activation energy will definitely keep the reaction at a lower rate.

Society uses the effects of temperature on reaction rate every day. Food storage is a prime example of how the temperature effect on reaction rate is utilized by society. Consumers store food in freezers and refrigerators to slow down the processes that cause it to spoil. The decrease in temperature decreases the rate at which food will break down or be broken down by bacteria. In the early years of the 20$^{\text{th}}$ century, explorers were fascinated with being the first to reach the South Pole. In order to attempt such a difficult task at a time without most of the technology that we take for granted today, they devised a variety of ways of surviving. One method was to store their food in the snow to be used later during their advances to the pole. On some explorations, they buried so much food that they didn't need to use all of it, and some was left behind. Many years later, when this food was located and thawed, it was found to still be edible.

When milk, for example, is stored in the refrigerator, the molecules in the milk have less energy. This means that while molecules will still collide with other molecules, few of them will react (which means in this case "spoil") because the molecules do not have sufficient energy to overcome the activation energy barrier. The molecules do have energy and are colliding, however, and so, over time, even in the refrigerator, the milk will spoil. Eventually the higher energy molecules will gain the energy needed to react and when enough of these reactions occur, the milk becomes "soured".

However, if that same carton of milk was at room temperature, the milk would react (in other words, "spoil") much more quickly. Most of the molecules would have sufficient energy to overcome the energy barrier at room temperature, and many more collisions would occur. This allows for the milk to spoil in a fairly short amount of time. This is also the reason why most fruits and vegetables ripen in the summer when the temperature is much warmer. You may have experienced this first hand if you have ever bitten into an unripe banana—it was probably sour tasting and might even have felt like biting into a piece of wood! When a banana ripens, numerous reactions occur that produce all the compounds that we expect to taste in a banana. But this can only happen if the temperature is high enough to allow these reactions to make those products.

## Effect of Concentration on Rate of Reaction

If you had an enclosed space, like a classroom, and there was one red ball and one green ball flying around the room in random motion, undergoing perfectly elastic collisions with the walls and with each other, in a given amount of time, the balls would collide with each other a certain number of times determined by probability. If you now put two red balls and one green ball in the room under the same conditions, the probability of a collision between a red ball and the green ball would exactly double. The green ball would have twice the chance of encountering a red ball in the same amount of time.

In terms of chemical reactions, a similar situation exists. Particles of two gaseous reactants or two reactants in solution have a certain probability of undergoing collisions with each other in a reaction vessel. If you double the concentration of either reactant, the probability of a collision doubles. The rate of reaction is proportional to the number of collisions per unit time. If one concentration is doubled, the number of collisions will also double. Assuming that the percent of collisions that are successful does not change, then having twice as many collisions will result in twice as many successful collisions. The rate of reaction is proportional to the number of collisions over time; increasing the concentration of either reactant increases the number of collisions, and therefore increases the number of successful collisions and the reaction rate.

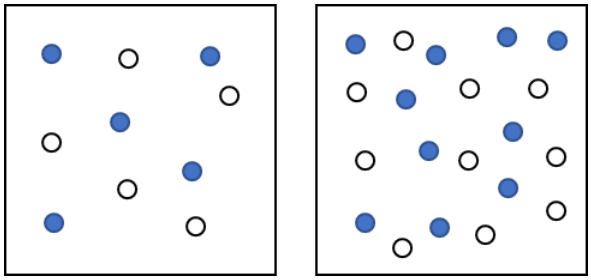


Figure 10.3.1: The left reaction container has a lower concentration than the right. In the right container, you can see that there are more opportunities for the reactants to collide because the concentration is higher.

For example, the chemical test used to identify a gas as oxygen, or not, relies on the fact that increasing the concentration of a reactant increases reaction rate. The reaction we call combustion refers to a reaction in which a flammable substance reacts with oxygen. If we light a wooden splint (a thin splinter of wood) on fire and then blow the fire out, the splint will continue to glow in air for a period of time. If we insert that glowing splint into any gas that does not contain oxygen, the splint will immediately cease to glow—that is, the reaction stops. Oxygen is the only gas that will support combustion, Air is approximately 20% oxygen gas. If we take that glowing splint and insert it into pure oxygen gas, the reaction will increase its rate by a factor of five, since pure oxygen has 5 times the concentration of oxygen that is in the air. When the reaction occurring on the glowing splint increases its rate by a factor of five, the glowing splint will suddenly burst back into full flame. This test, of thrusting a glowing splint into a gas, is used to identify the gas as oxygen. Only a greater concentration of oxygen than that found in air will cause the glowing splint to burst into flame.

### Catalysts

The rates of some chemical reactions can be increased dramatically by introducing certain other substances into the reaction mixture. Hydrogen peroxide is used as a disinfectant for scrapes and cuts, and it can be found in many medicine cabinets as a 3% aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese (IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** *is a substance that increases the rate of a chemical reaction without being used up in the reaction*. It accomplishes this task by

providing an alternate reaction pathway that has a lower activation energy barrier. After the reaction occurs, a catalyst returns to its original state, so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$2H_2O_2\,(aq) \overset{MnO_2}{\rightarrow} 2H_2O\,(l) + O_2\,(g) \tag{10.3.1}$$

A catalyst works by changing the mechanism of the reaction, which can be thought of as the specific set of smaller steps by which the reactants become products. The important point is that the use of a catalyst lowers the overall activation energy of the reaction (see figure below). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions, and the reaction rate increases.

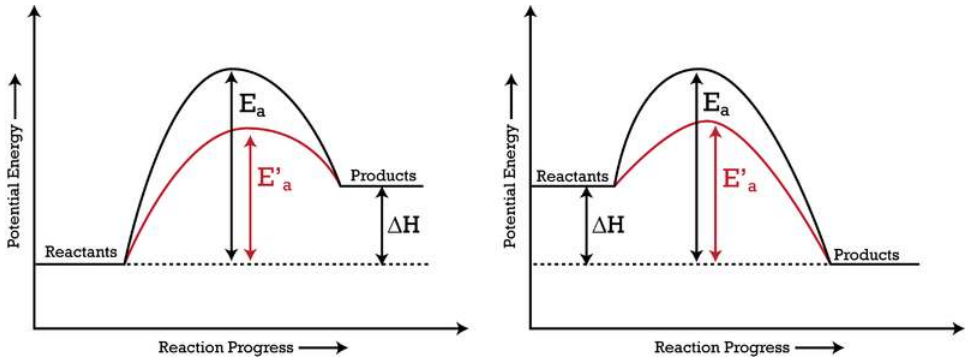



Figure **10.3.2**: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by $E_a$, while the catalyzed reaction is shown by $E'_a$. The heat of reaction $(\Delta H)$ is unchanged by the presence of the catalyst.

Catalysts are extremely important parts of many chemical reactions. Enzymes in your body act as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

## Contributors and Attributions

- 
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# 10.4: Dynamic Equilibrium

**Learning Objectives**

- Describe and identify reversible reactions.
- Define chemical equilibrium and identify when a reaction has reached equilibrium.

In the previous sections, 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.

## Reversible Reactions

A **reversible reaction** is one where the forward and reverse reaction happens at the same time. Consider the following reaction occurring in a closed container (so that no material can go in or out):

$$H_2 + I_2 \rightarrow 2HI$$

This is simply the reaction between elemental hydrogen and elemental iodine to make hydrogen iodide. The way the equation is written, we are led to believe that the reaction goes to completion, that all the $H_2$ and the $I_2$ react to make HI.

However, this is not the case. The reverse chemical reaction is also taking place:

$$2HI \rightarrow H_2 + I_2$$

It acts to undo what the first reaction does. Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow, like this:

$$H_2 + I_2 \rightleftharpoons 2HI$$

The *double arrow* implies that the reaction is going in both directions. Note that the reaction must still be balanced. So how do we know when these reactions stop, and can we predict the amount of products and reactants when the reaction is over?

## Dynamic Equilibrium



Figure **10.4.1**: 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 10.4.1). The reaction can be followed visually because the product ($NO_2$) is colored, whereas the reactant ( $N_2O_4$) is colorless:

$$\underset{\textit{colorless}}{N_2O_4(g)} \rightleftharpoons \underset{\textit{red–brown}}{2\,NO_2(g)} \tag{10.4.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4(g) \longrightarrow 2\,NO_2(g) \tag{10.4.2}$$

and reverse reaction

$$2\,NO_2(g) \longrightarrow N_2O_4(g) \tag{10.4.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is at equilibrium.

Figure 10.4.2 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 10.4.2*a*), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 10.4.2*b*). Thus equilibrium can be approached from either direction in a chemical reaction.

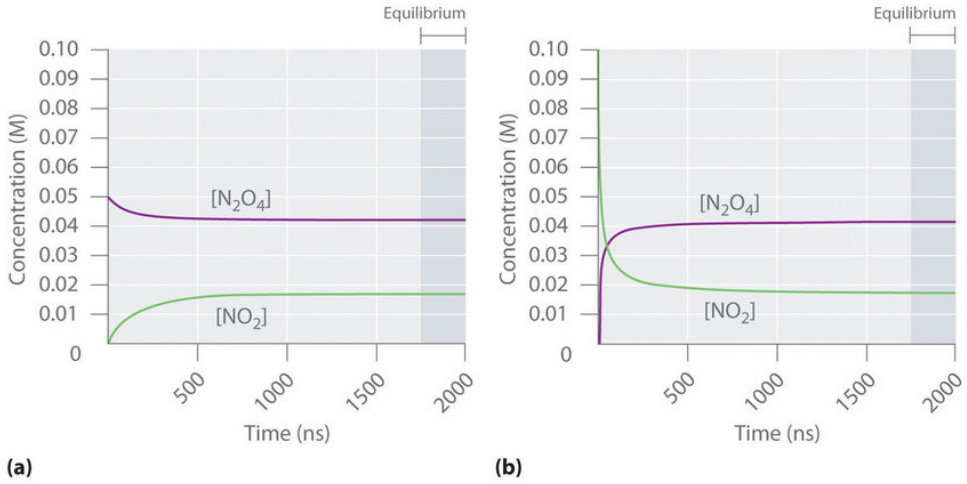



Figure 10.4.2: The Composition of $N_2O_4/NO_2$ Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous $N_2O_4$ and no gaseous $NO_2$. The concentration of $N_2O_4$ decreases with time as the concentration of $NO_2$ increases. (b) Initially, 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 10.4.3 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 10.4.1 and 10.4.2). 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.

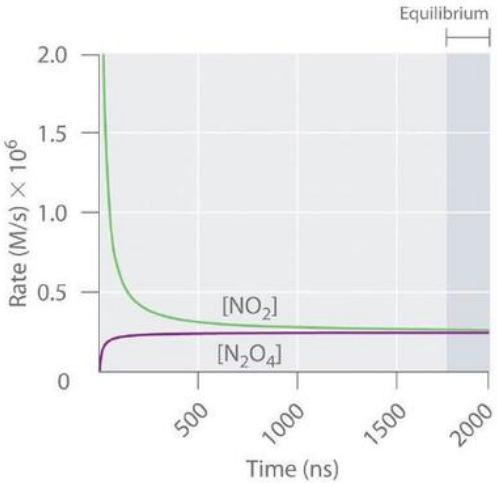



Figure **10.4.3**: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure **10.4.2**. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of $\mathbf{NO_2}$ (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of $\mathbf{N_2O_4}$ is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the $\mathbf{N_2O_4}$ 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 $\mathbf{N_2O_4}$ and $\mathbf{NO_2}$ no longer change.

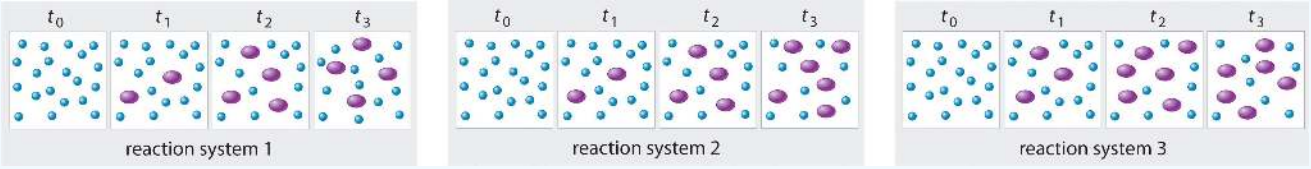
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

## Example 10.4.1

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?




**Given**: three reaction systems

**Asked for:** relative time to reach chemical equilibrium

**Strategy**:

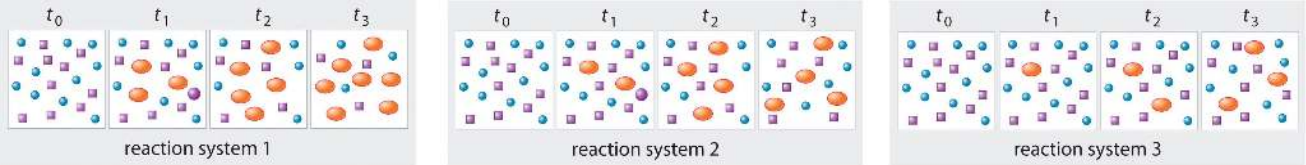
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

**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 10.4.1

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?




**Answer**

system 2



A Video Introduction to Dynamic Equilibrium: https://youtu.be/4AJbFuzW2cs

## 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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# 10.5: The Equilibrium Constant Expression

**Learning Objectives**

- Describe equilibrium constants.
- To write an equilibrium constant expression for any reaction.
- Compare the extent to which a reaction proceeds towards the products using equilibrium constants.

Is a system where the forward and reverse reaction happen at the same time, how do we predict the concentrations, or amounts, or products and reactants when the reaction reaches equilibrium? The rate of the forward and reverse reactions are equal when equilibrium is reached, and the ratio of products to reactants is constant. In equilibrium, we call this ratio the equilibrium constant.

## 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

$$aA + bB \rightleftharpoons cC + dD \tag{10.5.1}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{10.5.2}$$

where $K$ is the equilibrium constant for the reaction. Equation 10.5.1 is called the equilibrium equation, and the right side of Equation 10.5.2 is called the equilibrium constant expression. The relationship shown in Equation 10.5.2 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

**Writing Equilibrium Constant Expressions**

There are some rules about writing equilibrium constant expressions that need to be learned:

1. The products are on top and the reactants are on the bottom.
2. Brackets are used around each species in the reaction to indicate concentration (molarity)
3. Concentrations of products are multiplied on the top of the expression. Concentrations of reactants are multiplied together on the bottom.
4. Coefficients in the equation become exponents in the equilibrium constant expression. When the coefficient is one, it is not written as an exponent.
5. Solids, liquids, and solvents are assigned a value of 1, so their concentrations do not affect the value of K.

The equilibrium constant can vary over a wide range of values. The values of $K$ shown in Table 10.5.1, 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 $1.6 \times 10^{33}$ 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 10.5.1: Equilibrium Constants for Selected Reactions*

| Reaction | Temperature (K) | Equilibrium Constant (K) |
|---|---|---|
| $S(s) + O_2(g) \rightleftharpoons SO_2(g)$ | 300 | $4.4 \times 10^{53}$ |
| $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ | 500 | $2.4 \times 10^{47}$ |
| $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ | 300 | $1.6 \times 10^{33}$ |
| $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ | 300 | $4.1 \times 10^{18}$ |
| $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ | 300 | $4.2 \times 10^{13}$ |
| $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ | 300 | $2.7 \times 10^{8}$ |
| $H_2(g) + D_2(g) \rightleftharpoons 2HD(g)$ | 100 | 1.92 |
| $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ | 300 | $2.9 \times 10^{-1}$ |
| $I_2(g) \rightleftharpoons 2I(g)$ | 800 | $4.6 \times^{10-7}$ |
| $Br_2(g) \rightleftharpoons 2Br(g)$ | 1000 | $4.0 \times 10^{-7}$ |
| $Cl_2(g) \rightleftharpoons 2Cl(g)$ | 1000 | $1.8 \times 10^{-9}$ |
| $F_2(g) \rightleftharpoons 2F(g)$ | 500 | $7.4 \times 10^{-13}$ |

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \tag{10.5.3}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{10.5.4}$$

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 10.5.1 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as

$$\text{reactants} \rightleftharpoons \text{products}. \tag{10.5.5}$$

When $K$ is a **large** number, the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $K$ is a very **small** number, the reaction produces almost no products as written. Systems for which $K$ is neither large nor small, the equilibrium will have significant concentrations of both reactants and products.

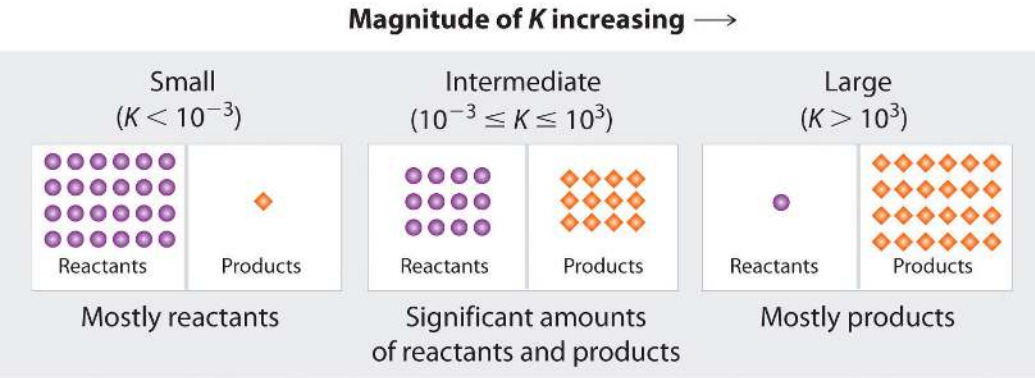



Figure **10.5.1**: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

A large value of the equilibrium constant $K$ means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

**Example 10.5.1**

Write the equilibrium constant expression for each reaction.

- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
- $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

**Given**: balanced chemical equations

**Asked for**: equilibrium constant expressions

**Strategy**:

Refer to Equation ???. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

**Solution**:

The only product is ammonia, which has a coefficient of 2. For the reactants, $N_2$ has a coefficient of 1 and H2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \tag{10.5.6}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are $CO$, with a coefficient of 1, and $O_2$, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{10.5.7}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for $O_2$. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2} \tag{10.5.8}$$

## Exercise 10.5.1

Write the equilibrium constant expression for each reaction.

a. $N_2O_{(g)} \rightleftharpoons N_{2(g)} + \frac{1}{2}O_{2(g)}$
b. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
c. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Answer:

a. $K = \dfrac{[N_2][O_2]^{1/2}}{[N_2O]}$
b. $K = \dfrac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$
c. $K = \dfrac{[HI]^2}{[H_2][I_2]}$

## Example 10.5.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

a. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
b. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
c. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
d. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

**Given**: systems and values of $K$

**Asked for**: composition of systems at equilibrium

**Strategy**:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

**Solution**:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

## Exercise 10.5.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{10.5.9}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

At which temperature would you expect to find the highest proportion of $H_2$ and $N_2$ in the equilibrium mixture?

Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

**Answer**:

a. 327°C, where $K$ is smallest
b. 25°C

The equilibrium constant expression is an equation that we can use to solve for $K$ or for the concentration of a reactant or product.

**Example 10.5.3**

Determine the value of $K$ for the reaction

$$SO_2\,(g) + NO_2\,(g) \rightleftharpoons SO_3\,(g) + NO\,(g)$$

when the equilibrium concentrations are: $[SO_2] = 1.20\ M$, $[NO_2] = 0.60\ M$, $[NO] = 1.6\ M$, and $[SO_3] = 2.2\ M$.

**Solution**

Step 1: Write the equilibrium constant expression:

$$K = \frac{[SO_3]\,[NO]}{[SO_2]\,[NO_2]}$$

Step 2: Substitute in given values and solve:

$$K = \frac{(2.2)\,(1.6)}{(1.20)\,(0.60)} = 4.9$$



Determining the Equilibrium Expression: https://youtu.be/ZK9cMIWFerY

## Summary

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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.

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10.5: The Equilibrium Constant Expression is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

- **15.4: The Equilibrium Constant - A Measure of How Far a Reaction Goes** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

# 10.6: Le Chatelier's Principle

**Learning Outcomes**

- Define Le Chatelier's principle.
- Predict how the change in amounts of substances, temperature, or pressure will affect amounts of reactants and products present at equilibrium.

## Le Chatelier's Principle

Chemical equilibrium was studied by the French chemist Henri Le Chatelier (1850 - 1936) and his description of how a system responds to a stress to equilibrium has become known as **Le Chatelier's principle**: When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentrations of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increase, while the concentrations of reactants decrease. When the reverse reaction is favored, the concentrations of the products decrease, while the concentrations of reactants increase.

| Original Equilibrium | Favored Reaction | Result |
|---|---|---|
| $\mathrm{A} \rightleftharpoons \mathrm{B}$ | Forward: $\mathrm{A} \rightarrow \mathrm{B}$ | [A] decreases; [B] increases |
| $\mathrm{A} \rightleftharpoons \mathrm{B}$ | Reverse: $\mathrm{A} \leftarrow \mathrm{B}$ | [A] increases; [B] decreases |



Figure 9.6.1: *Henri Le Chatelier*.

## Effect of Concentration

A change in concentration of one of the substances in an equilibrium system typically involves either the addition or the removal of one of the reactants or products. Consider the Haber-Bosch process for the industrial production of ammonia from nitrogen and hydrogen gases.

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightleftharpoons 2\mathrm{NH_3}\,(g)$$

If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that removes that substance. When more $\mathrm{N_2}$ is added, the forward reaction will be favored because the forward reaction uses up $\mathrm{N_2}$ and converts it to $\mathrm{NH_3}$. The forward reaction speeds up temporarily as a result of the addition of a reactant. The position of equilibrium shifts as more $\mathrm{NH_3}$ is produced. The concentration of $\mathrm{NH_3}$ increases, while the concentrations of $\mathrm{N_2}$ and $\mathrm{H_2}$ decrease. After some time passes, equilibrium is reestablished with new concentrations of all three substance. As can be seen in the figure below, if more $\mathrm{N_2}$ is added, a new equilibrium is achieved by the system. The new concentration of $\mathrm{NH_3}$ is higher because of the favoring of the forward reaction. The new concentration of the $\mathrm{H_2}$ is lower .The concentration of $\mathrm{N_2}$ is higher than in the original equilibrium, but went down slightly following the addition of the $\mathrm{N_2}$ that disturbed the original equilibrium. By responding in this way, the value of the equilibrium constant for the reaction, $K_{\mathrm{eq}}$, does not change as a result of the stress to the system.

In other words, the amount of each substance is different but the ratio of the amount of each remains the same.

If more $\mathrm{NH_3}$ were added, the reverse reaction would be favored. This "favoring" of a reaction means temporarily speeding up the reaction in that direction until equilibrium is reestablished. Recall that once equilibrium is reestablished, the rates of the forward and reverse reactions are again equal. The addition of $\mathrm{NH_3}$ would result in increased formation of the reactants, $\mathrm{N_2}$ and $\mathrm{H_2}$.

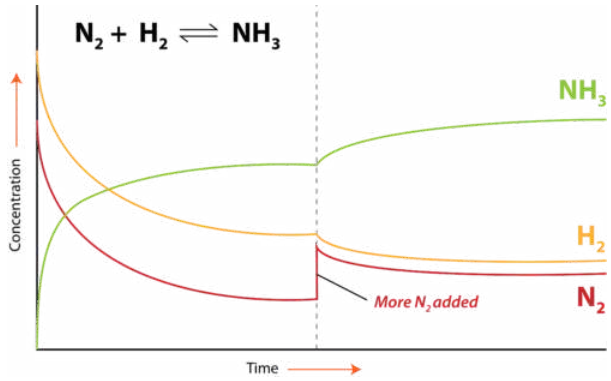



Figure 9.6.2: *The Haber-Bosch process is an equilibrium between reactants* $\mathbf{N_2}$ *and* $\mathbf{H_2}$ *and product* $\mathbf{NH_3}$.

An equilibrium can also be disrupted by the removal of one of the substances. If the concentration of a substance is decreased, the system will respond by favoring the reaction that replaces that substance. In the industrial Haber-Bosch process, $\mathbf{NH_3}$ is removed from the equilibrium system as the reaction proceeds. As a result, the forward reaction is favored so that more $\mathbf{NH_3}$ is produced. The concentrations of $\mathbf{N_2}$ and $\mathbf{H_2}$ decrease. Continued removal of $\mathbf{NH_3}$ will eventually force the reaction to go to completion until all of the reactants are used up. If either $\mathbf{N_2}$ or $\mathbf{H_2}$ were removed from the equilibrium system, the reverse reaction would be favored and the concentration of $\mathbf{NH_3}$ would decrease.

The effect of changes in concentration on an equilibrium system according to Le Chatelier's principle is summarized in the table below.

Table 9.6.1

| Stress | Response |
|---|---|
| addition of reactant | forward reaction favored |
| addition of product | reverse reaction favored |
| removal of reactant | reverse reaction favored |
| removal of product | forward reaction favored |

**Example 10.6.1**

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

How will it affect the reaction if the equilibrium is stressed by each change?

1. $H_2$ is added.
2. $NH_3$ is added.
3. $NH_3$ is removed.

**Solution**

1. If $H_2$ is added, there is now more reactant, so the reaction will shift to the right (toward products) to reduce the added $H_2$.
2. If $NH_3$ is added, there is now more product, so the reaction will shift to the left (toward reactants) to reduce the added $NH_3$.
3. If $NH_3$ is removed, there is now less product, so the reaction will shift to the right (toward products) to replace the product removed.

**10.6.1 Exercise**

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

How will it affect the reaction if the equilibrium is stressed by each change?

1. $Br_2$ is removed.
2. $COBr_2$ is added.

**Answer**

1. shift to the left (toward reactants)
2. shift to the left (toward reactants)

## Effect of Temperature

Increasing or decreasing the temperature of a system at equilibrium is also a stress to the system. The equation for the Haber-Bosch process is written again below, as a thermochemical equation (i.e. it contains information about the energy gained or lost when the reaction occurs).

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightleftharpoons 2\mathrm{NH_3}\,(g) + 91\ \mathrm{kJ}$$

The forward reaction is the exothermic direction: the formation of $\mathrm{NH_3}$ releases heat which is why that is shown as a product. The reverse reaction is the endothermic direction: as $\mathrm{NH_3}$ decomposes to $\mathrm{N_2}$ and $\mathrm{H_2}$, heat is absorbed. An increase in the temperature for this is like adding a product because heat is being released by the reaction. If we add a product then the reaction proceeds towards the formation of more reactants. Reducing the temperature for this system would be similar to removing a product which would favor the formation of more products. The amount of $\mathrm{NH_3}$ will increase and the amount of $\mathrm{N_2}$ and $\mathrm{H_2}$ will decrease.

For changes in concentration, the system responds in such a way that the value of the equilibrium constant, $K_{eq}$ is unchanged. However, a change in temperature shifts the equilibrium and the $K_{eq}$ value either increases or decreases. As discussed in the previous section, values of $K_{eq}$ are dependent on the temperature. When the temperature of the system for the Haber-Bosch process is increased, the resultant shift in equilibrium towards the reactants means that the $K_{eq}$ value decreases. When the temperature is decreased, the shift in equilibrium towards the products means that the $K_{eq}$ value increases.

Le Chatelier's principle as related to temperature changes can be illustrated easily be the reaction in which dinitrogen tetroxide is in equilibrium with nitrogen dioxide.

$$\mathrm{N_2O_4}\,(g) + \mathrm{heat} \rightleftharpoons 2\mathrm{NO_2}\,(g)$$

Dinitrogen tetroxide ($\mathrm{N_2O_4}$) is colorless, while nitrogen dioxide ($\mathrm{NO_2}$) is dark brown in color. When $\mathrm{N_2O_4}$ breaks down into $\mathrm{NO_2}$, heat is absorbed (endothermic) according to the forward reaction above. Therefore, an increase in temperature (adding heat) of the system will favor the forward reaction. Conversely, a decrease in temperature (removing heat) will favor the reverse reaction.

### ✔ Example 10.6.2

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ$$

**Solution**

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts to the left (back toward reactants).

### 10.6.2 Exercise

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

**Answer**

Equilibrium shifts to the left (toward reactants).

## Effect of Pressure

Changing the pressure of an equilibrium system in which gases are involved is also a stress to the system. A change in the pressure on a liquid or a solid has a negligible effect. We will return again the equilibrium for the Haber-Bosch process. Imagine the gases are contained in a closed system in which the volume of the system is controlled by an adjustable piston as shown in the figure below.

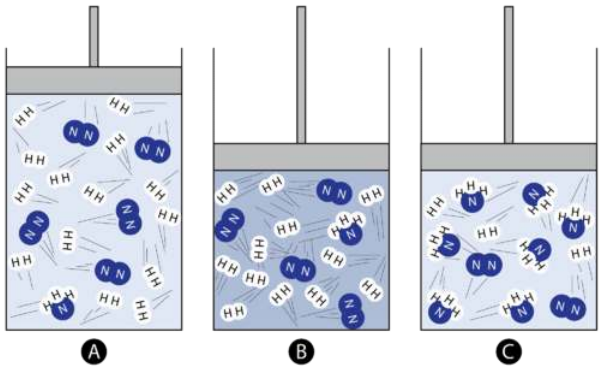



Figure 9.6.3: *Effect of pressure on equilibrium. (A) is at equilibrium, (B) increase of pressure through decreased volume, and (C) equilibrium is reestablished.*

On the far left, the reaction system contains primarily $\mathbf{N_2}$ and $\mathbf{H_2}$, with only one molecule of $\mathbf{NH_3}$ present. As the piston is pushed inwards, the pressure of the system increases according to Boyle's law. This is a stress to the equilibrium. In the middle image, the same number of molecules is now confined in a smaller space and so the pressure has increased. According to Le Chatelier's principle, the system responds in order to relieve the stress. In the image on the right, the forward reaction has been favored and more $\mathbf{NH_3}$ is produced. The overall result is a decrease in the number of gas molecules in the entire system. This in turn decreases the pressure and provides a relief to the original stress of a pressure increase. An increase in pressure on an equilibrium system favors the reaction which products fewer total moles of gas. In this case, it is the forward reaction that is favored.

A decrease in pressure on the above system could be achieved by pulling the piston outward, increasing the container volume. The equilibrium would respond by favoring the reverse reaction in which $\mathbf{NH_3}$ decomposes to $\mathbf{N_2}$ and $\mathbf{H_2}$. This is because the overall number of gas molecules would increase and so would the pressure. A decrease in pressure on an equilibrium system favors the reaction which produces more total moles of gas. This is summarized in the table below.

Table 9.6.2

| Stress | Response |
|---|---|
| pressure increase | reaction produces fewer gas molecules |
| pressure decrease | reaction produces more gas molecules |

Like changes in concentration, the $K_{eq}$ value for a given reaction is unchanged by a change in pressure. The amounts of each substance will change but the ratio will not. It is important to remember when analyzing the effect of a pressure change on equilibrium that only gases are affected. If a certain reaction involves liquids or solids, they should be ignored. For example, calcium carbonate decomposes according to the equilibrium reaction:

$$\mathrm{CaCO_3}\,(s) \rightleftharpoons \mathrm{CaO}\,(s) + \mathrm{O_2}\,(g)$$

Oxygen is the only gas in the system. An increase in the pressure of the system slows the rate of decomposition of $\mathbf{CaCO_3}$ because the reverse reaction is favored. When a system contains equal moles of gas on both sides of the equation, pressure has no effect on the equilibrium position, as in the formation of $\mathbf{HCl}$ from $\mathbf{H_2}$ and $\mathbf{Cl_2}$.

$$\mathrm{H_2}\,(g) + \mathrm{Cl_2}\,(g) \rightleftharpoons 2\mathrm{HCl}\,(g)$$

**Example 10.6.3**

What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

**Solution**

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts to the right (toward the products side).

**10.6.3 Exercise**

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

**Answer**

Reaction shifts to the left (toward reactants).

## Application of Le Chatelier's Principle

**Oxygen transport by the blood**

In aerobic respiration, oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.

hemoglobin + $O_2$ $\rightleftharpoons$ oxyhemoglobin

The partial pressure of $O_2$ in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the $O_2$ concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

## Key Takeaways

- In a reaction at equilibrium, the introduction of more products will shift the mass balance towards more reactants, and the introduction of more reactants will lead to the formation of more products, but the *ratio* of *Products/Reactants* (*equilibrium constant*), *K* is unchanged.
- If temperature is changed, the numeric value *K* will change. If a reaction is *exothermic* (releases heat), an increase in the **temperature** will force the equilibrium to the left, causing the system to absorb heat and thus partially offsetting the rise in temperature. The opposite effect occurs for *endothermic* reactions, which are shifted to the right by rising temperature.
- The effect of **pressure** on an equilibrium is significant only for reactions which involve different numbers of moles of gases on the two sides of the equation. An increase in the total pressure will shift to the side with fewer moles of gas. A decrease in pressure will shift to the side with more moles of gas.

## Contributors and Attributions

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# CHAPTER OVERVIEW

## 11: Acids and Bases

Acids and bases are common substances found in many every day items, from fruit juices and soft drinks to soap. In this chapter, we will examine the properties of acids and bases, and learn about the chemical nature of these important compounds. We will cover pH, and how to calculate the pH of a solution.


11.1: Acids- Properties and Examples

11.1.1: Naming Acids

11.2: Bases- Properties and Examples

11.3: Molecular Definitions of Acids and Bases

11.4: Reactions of Acids and Bases

11.5: Strong and Weak Acids and Bases

11.6: Water - Acid and Base in One

11.7: The pH and pOH Scales - Ways to Express Acidity and Basicity

11.8: Buffer Solutions

11.9: Acid–Base Titration


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# 11.1: Acids- Properties and Examples

**Learning Objectives**

- Examine properties of acids.
- Identify common acids and bases.

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible coffee.

## Acids

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicates. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g) \tag{11.1.1}$$

5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

It should not be hard for you to name several common acids (but you might find that listing bases is a little more difficult). Below is a partial list of some common acids, along with some chemical formulas:

Table **11.1.1**: Common Acids and Their Uses

| Chemist Name | Common Name | Uses |
|---|---|---|
| hydrochloric acid, HCl | muriatic acid (used in pools) and stomach acid is HCl | Used in cleaning (refining) metals, in maintenance of swimming pools, and for household cleaning. |
| sulfuric acid, $H_2SO_4$ | | Used in car batteries, and in the manufacture of fertilizers. |
| nitric acid, $HNO_3$ | | Used in the manufacture of fertilizers, explosives and in extraction of gold. |
| acetic acid, $HC_2H_3O_2$ | vinegar | Main ingredient in vinegar. |
| carbonic acid, $H_2CO_3$ | responsible for the "fizz" in carbonated drinks | As an ingredient in carbonated drinks. |
| citric acid, $C_6H_8O_7$ | | Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions. |
| acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$ | aspirin | The active ingredient in aspirin. |

What exactly makes an acid an acid, and what makes a base act as a base? Take a look at the formulas given in the above table and take a guess.

## Hydrochloric Acid

Hydrochloric acid is a corrosive, strong mineral acid with many industrial uses. A colorless, highly pungent solution of hydrogen chloride (HCl) in water. Hydrochloric acid is usually prepared by treating $\mathbf{HCl}$ with water.

$$\mathbf{HCl\,(g) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$

Hydrochloric acid can therefore be used to prepare chloride salts. Hydrochloric acid is a strong acid, since it is completely dissociated in water. Hydrochloric acid is the preferred acid in titration for determining the amount of bases.

## Sulfuric Acid

Sulfuric acid is a highly corrosive strong mineral acid with the molecular formula $\mathbf{H_2SO_4}$. Sulfuric acid is a diprotic acid and has a wide range of applications including use in domestic acidic drain cleaners,[1] as an electrolyte in lead-acid batteries, and in various cleaning agents. It is also a central substance in the chemical industry.



Figure **11.1.1**: Drops of concentrated sulfuric acid rapidly decompose a piece of cotton towel by dehydration. (CC BY-SA 3.0; Toxic Walker).

Because the hydration of sulfuric acid is thermodynamically favorable (and is highly exothermic) and the affinity of it for water is sufficiently strong, sulfuric acid is an excellent dehydrating agent. Concentrated sulfuric acid has a very powerful dehydrating

property, removing water ($H_2O$) from other compounds including sugar and other carbohydrates and producing carbon, heat, steam. Sulfuric acid behaves as a typical acid in its reaction with most metals by generating hydrogen gas (Equation 11.1.2).

$$M + H_2SO_4 \longrightarrow M(SO_4) + H_2 \tag{11.1.2}$$

## Nitric Acid

Nitric acid ($HNO_3$) is a highly corrosive mineral acid and is also commonly used as a strong oxidizing agent. Nitric acid is normally considered to be a strong acid at ambient temperatures. Nitric acid can be made by reacting nitrogen dioxide ($NO_2\,(g)$) with water.

$$3\,NO_2\,(g) + H_2O\ (l) \longrightarrow 2\,HNO_3\,(ag) + NO\,(g)$$

Nitric acid reacts with most metals, but the details depend on the concentration of the acid and the nature of the metal. Dilute nitric acid behaves as a typical acid in its reaction with most metals (e.g., nitric acid with magnesium, manganese or zinc will liberate $H_2$ gas):

$$Mg + 2\,HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

$$Mn + 2\,HNO_3 \longrightarrow Mn(NO_3)_2 + H_2$$

$$Zn + 2\,HNO_3 \longrightarrow Zn(NO_3)_2 + H_2$$

Nitric acid is a corrosive acid and a powerful oxidizing agent. The major hazard it poses is chemical burn, as it carries out acid hydrolysis with proteins (amide) and fats (ester) which consequently decomposes living tissue (Figure 11.1.2). Concentrated nitric acid stains human skin yellow due to its reaction with the keratin



Figure 11.1.2: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

## Carbonic Acid

Carbonic acid is a chemical compound with the chemical formula $H_2CO_3$ and is also a name sometimes given to solutions of carbon dioxide in water (carbonated water), because such solutions contain small amounts of $H_2CO_3\,(aq)$. Carbonic acid, which is a weak acid, forms two kinds of salts: the carbonates and the bicarbonates. In geology, carbonic acid causes limestone to dissolve, producing calcium bicarbonate—which leads to many limestone features such as stalactites and stalagmites. Carbonic acid is a polyprotic acid, specifically it is diprotic, meaning that it has two protons which may dissociate from the parent molecule.

When carbon dioxide dissolves in water, it exists in chemical equilibrium (discussed in Chapter 15), producing carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

The reaction can be pushed to favor the reactants to generate $CO_2\,(g)$ from solution, which is key to the bubbles observed in carbonated beverages (Figure 11.1.3).



Figure 11.1.3: A glass of sparkling water. (CC BY-SA 3.0; Nevit Dilmen).

## Formic Acid

Formic acid ($HCO_2H$) is the simplest carboxylic acid and is an important intermediate in chemical synthesis and occurs naturally, most notably in some ants. The word "formic" comes from the Latin word for ant, formica, referring to its early isolation by the distillation of ant bodies. Formic acid occurs widely in nature as its conjugate base formate.

## Citric Acid

Citric acid ($C_6H_8O_7$) is a weak organic tricarboxylic acid that occurs naturally in citrus fruits. The citrate ion is an intermediate in the TCA cycle (Krebs cycle), a central metabolic pathway for animals, plants and bacteria. Because it is one of the stronger edible acids, the dominant use of citric acid is used as a flavoring and preservative in food and beverages, especially soft drinks.

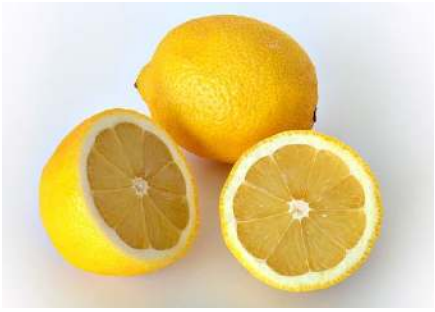


Figure 11.1.4: Lemons, oranges, limes, and other citrus fruits possess high concentrations of citric acid (CC BY-SA 2.5; André Karwath).

## Acetylsalicylic Acid

Acetylsalicylic acid (also known as aspirin) is a medication used to treat pain, fever, and inflammation. Aspirin, in the form of leaves from the willow tree, has been used for its health effects for at least 2,400 years.

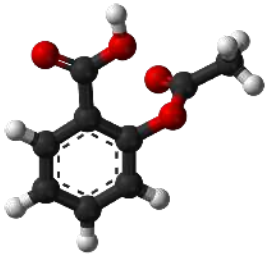


Figure 11.1.5: Ball-and-stick model of the aspirin molecule. (Public Domain; Ben Mills).

Aspirin is a white, crystalline, weakly acidic substance.

## Summary

A brief summary of key aspects of several acids commonly encountered by students was given. Acids are a distinct class of compounds because of the properties of their aqueous solutions.

## Contributions & Attributions

- 
- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

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# 11.1.1: Naming Acids

**Learning Objectives**

- Use nomenclature to name common acids

A spot test for gold has been in use for decades. The sample is first treated with nitric acid. Other metals may react or dissolve in this acid, but gold will not. Then the sample is added to a mixture of nitric acid and hydrochloric acid. Gold will only dissolve in this mixture. The term "acid test" arose from the California gold rush in the late 1840's when this combination was used to test for the presence of real gold. It has since come to mean, "tested and approved" in a number of fields.

## Acids

An **acid** can be defined in several ways. The most straightforward definition is that an acid is a molecular compound that contains one or more hydrogen atoms and produces hydrogen ions ($\mathbf{H^+}$) when dissolved in water.




Figure **11.1.1.1**: (A) Vinegar comes in a variety of types, but all contain acetic acid. (B) Citrus fruits like grapefruit contain citric and ascorbic acids.

This is a different type of compound than the others we have seen so far. Acids are molecular, which means that in their pure state they are individual molecules and do not adopt the extended three-dimensional structures of ionic compounds like $\mathbf{NaCl}$. However, when these molecules are dissolved in water, the chemical bond between the hydrogen atom and the rest of the molecule breaks, leaving a positively-charged hydrogen ion and an anion. This can be symbolized in a chemical equation:

$$\mathbf{HCl \rightarrow H^+ + Cl^-}$$

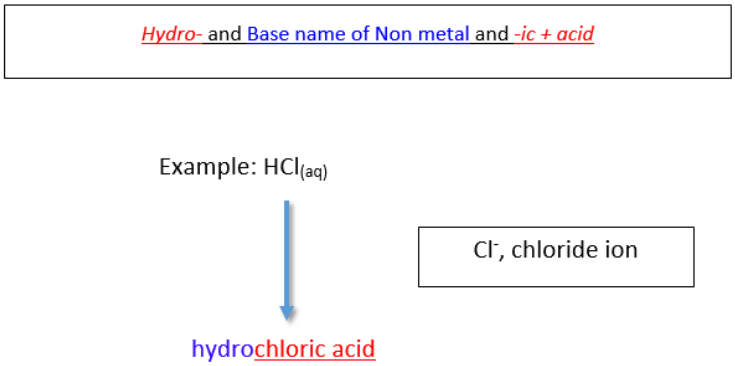
Since acids produce $\mathbf{H^+}$ cations upon dissolving in water, the $\mathbf{H}$ of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the $\mathbf{H}$) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here.

## Naming Acids

Since all acids contain hydrogen, the name of an acid is based on the anion that goes with it. These anions can either be monatomic or polyatomic.

### Naming Binary acids (in aqueous form)

A **binary acid** is an acid that consists of hydrogen and one other element. The most common binary acids contain a halogen. The acid name begins with the prefix *hydro-*. followed by the base name of the anion, followed by the suffix *-ic*.



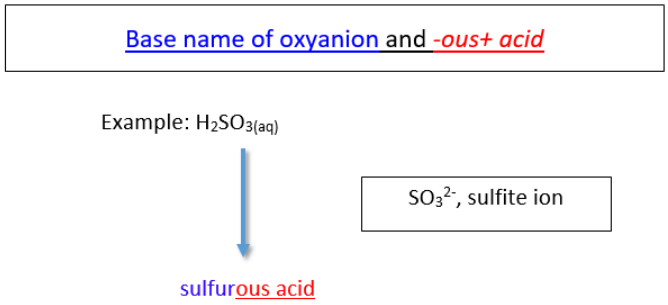

Formula for naming acids: Hydro- and Base name of nonmetal and -ic + acid. Example: HCl is hydrochloric acid.

## Naming Oxyacids

An **oxyacid** is an acid that consists of hydrogen, oxygen, and a third element. The third element is usually a nonmetal.

a. Oxyanions with ***-ite*** ending.

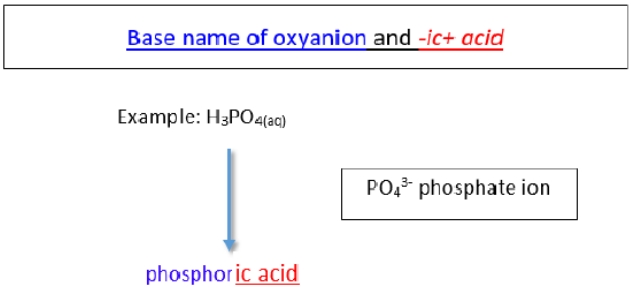
The name of the acid is the root of the anion followed by the suffix ***-ous***. There is no prefix.




Formula for naming oxyanions with -ite ending: Base name of oxyanion and -ous + acid. Example: H2SO3 is sulfurous acid.

b. Oxyanions with ***-ate*** ending.

The name of the acid is the root of the anion followed by the suffix ***-ic***. There is no prefix.



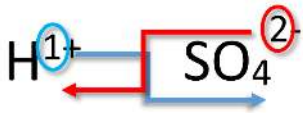

Formula for naming oxyanions with -ate ending: Base name of oxyanion and -ic + acid. Example: H3PO4 is phosphoric acid.

**Note**

The base name for sulfur containing oxyacid is ***sulfur-*** instead of just ***sulf-***. The same is true for a phosphorus containing oxyacid. The base name is ***phosphor-*** instead of simply ***phosph-***.

## Writing Formulas for Acids

Like other compounds that we have studied, acids are electrically neutral. Therefore, the charge of the anion part of the formula must be exactly balanced out by the $\mathbf{H^+}$ ions. Another way to think about writing the correct formula is to utilize the crisscross method, shown below for sulfuric acid.




H2SO4: H has +1 charge and SO4 has -2 charge, so there must be 2 H+ and 1 SO4 for the charges to balance out.

Formula: $H_2SO_4$

***Figure* 11.1.1.2*:*** *Crisscross approach to writing formula for sulfuric acid.*

## Summary

- Acids are molecular compounds that release hydrogen ions.
- A binary acid consists of hydrogen and one other element.
- Oxyacids contain hydrogen, oxygen, and one other element.
- The name of the acid is based on the anion attached to the hydrogen.

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# 11.2: Bases- Properties and Examples

**Learning Objectives**

- Examine properties of bases.

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the **HCl** in the stomach and neutralize it, taking care of that unpleasant feeling.

## Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base, while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.



Figure **11.2.1**: Phenolphthalein indicator in presence of base.

**Warning!**

Tasting chemicals and touching them are NOT good lab practices and should be avoided—in other words—don't do this at home.

Bases are less common as foods, but they are nonetheless present in many household products. Many cleaners contain ammonia, a base. Sodium hydroxide is found in drain cleaner. **Antacids**, which combat excess stomach acid, are comprised of bases such as magnesium hydroxide or sodium hydrogen carbonate. Various common bases and corresponding uses are given in Table **11.2.2**.

Table **11.2.1**: Common Bases and Corresponding Uses

| Some Common Bases | Uses |
|---|---|
| sodium hydroxide, NaOH (lye or caustic soda) | Used in the manufacture of soaps and detergents, and as the main ingredient in oven and drain cleaners. |
| potassium hydroxide, KOH (lye or caustic potash) | Used in the production of liquid soaps and soft soaps. Used in alkaline batteries. |
| magnesium hydroxide, $Mg(OH)_2$ (milk of magnesia) | Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater. |
| calcium hydroxide, $Ca(OH)_2$ (slaked lime) | Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil. |
| aluminum hydroxide | Used in water purification and as an ingredient in antacids. |
| ammonia, $NH_3$ | Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers. |

## Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is an inorganic compound with formula $\mathbf{NaOH}$. It is a white solid ionic compound consisting of sodium cations $\mathbf{Na^+}$ and hydroxide anions $\mathbf{OH^-}$.

Dissolution of solid sodium hydroxide in water is a highly exothermic reaction:

$$\mathbf{NaOH\,(s) \rightarrow Na^+\,(aq) + OH^-\,(aq)}$$

The resulting solution is usually colorless and odorless and feels slippery when it comes in contact with skin.



Figure **11.2.1**: Sample of sodium hydroxide as pellets in a watch glass. (Public Domain; Walkerma.)

## Potassium Hydroxide

Potassium hydroxide is an inorganic compound with the formula $\mathbf{KOH}$, and is commonly called caustic potash. Along with sodium hydroxide (NaOH), this colorless solid is a prototypical strong base. It has many industrial and niche applications, most of which exploit its corrosive nature and its reactivity toward acids. Its dissolution in water is strongly exothermic.

$$\mathbf{KOH\,(s) \rightarrow K^+\,(aq) + OH^-\,(aq)}$$

Concentrated aqueous solutions are sometimes called *potassium lyes*.

## Magnesium Hydroxide

Magnesium hydroxide is the inorganic compound with the chemical formula $\mathbf{Mg(OH)_2}$. Magnesium hydroxide is a common component of antacids, such as milk of magnesia, as well as laxatives.




Figure 11.2.1: Bottle of Antacid tablets. (CC BY 2.,5; Midnightcomm).

It is a white solid with low solubility in water. Combining a solution of many magnesium salts with basic water induces precipitation of solid $\mathbf{Mg(OH)_2}$. However, a weak concentration of dissociated ions can be found in solution:

$$\mathrm{Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,OH^-\,(aq)}$$

## Calcium Hydroxide

Calcium hydroxide (traditionally called slaked lime) is an inorganic compound with the chemical formula $\mathbf{Ca(OH)_2}$. It is a colorless crystal or white powder. It has many names including hydrated lime, caustic lime, builders' lime, slaked lime, cal, or pickling lime. Calcium hydroxide is used in many applications, including food preparation. Limewater is the common name for a saturated solution of calcium hydroxide.

Calcium hydroxide is relatively insoluble in water, but is large enough that its solutions are basic according to the following reaction:

$$\mathrm{Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,OH^-\,(aq)}$$

## Ammonia

Ammonia is a compound of nitrogen and hydrogen with the formula $\mathbf{NH_3}$ and is a colorless gas with a characteristic pungent smell. It is the active product of “smelling salts,” and can quickly revive the faint of heart and light of head. Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.

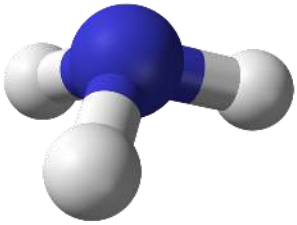


Figure 11.2.1: Ball-and-stick model of the ammonia molecule. (Public Domain; Ben Mills).

In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from $\mathbf{H_2O}$ to yield ammonium and hydroxide ions:

$$\mathrm{NH_3\,(g) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)}$$

Ammonia is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products.

## Summary

- A brief summary of properties of bases was given.
- The properties of bases mostly contrast those of acids.
- Bases have many, varied uses.

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# 11.3: Molecular Definitions of Acids and Bases

**Learning Objectives**

- Identify an Arrhenius acid and an Arrhenius base.
- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

There are three major classifications of substances known as acids or bases. The theory developed by Svante Arrhenius in 1883, the Arrhenius definition, states that an acid produces $H^+$ in solution and a base produces $OH^-$. Later, two more sophisticated and general theories were proposed. These theories are the Brønsted-Lowry and Lewis definitions of acids and bases. This section will cover the Arrhenius and Brønsted-Lowry theories; the Lewis theory is discussed elsewhere.

## The Arrhenius Theory 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. 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 completely into hydrogen ($H^+$) and chlorine ($Cl^-$) ions when dissolved in water, thereby releasing $H^+$ ions into solution. Formation of the hydronium ion equation:

$$HCl\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + Cl^-\,(aq)$$

An **Arrhenius base** is a compound that **increases the concentration of $OH^-$ ions** that are present when added to water. The dissociation is represented by the following equation:

$$NaOH\ \ (aq) \rightarrow Na^+\ \ (aq) + OH^-\ \ (aq)$$

In this reaction, sodium hydroxide (NaOH) disassociates into sodium ($Na^+$) and hydroxide ($OH^-$) ions when dissolved in water, thereby releasing $OH^-$ ions into solution.

> *Arrhenius acids are substances which produce hydrogen ions in solution and Arrhenius bases are substances which produce hydroxide ions in solution.*

**Limitations to the Arrhenius Theory**

The Arrhenius theory has many more limitations than the other two theories. The theory does not explain the weak base ammonia ($NH_3$), which in the presence of water, releases hydroxide ions into solution, but does not contain OH- itself. The Arrhenius definition of acid and base is also limited to aqueous (i.e., water) solutions.

## The Brønsted-Lowry Theory of Acids and Bases

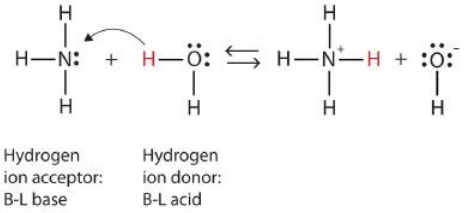
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton ($H^+$) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, **a Brønsted-Lowry acid** is a **proton donor (PD)**, while **a Brønsted-Lowry base** is a **proton acceptor (PA)**.

> *A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.*

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_3\,(aq) + H_2O\,(\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \tag{11.3.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:

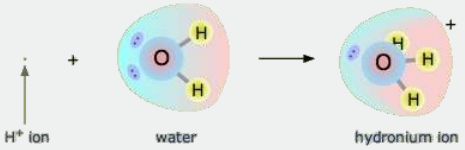



Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the $H^+$ ion attaches itself to $H_2O$ to make $H_3O^+$, which is called the *hydronium ion*. For most purposes, $H^+$ and $H_3O^+$ represent the same species, but writing $H_3O^+$ instead of $H^+$ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

### The Hydronium Ion

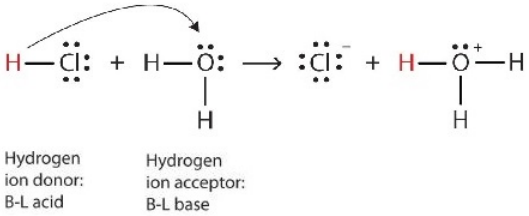
A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than $H_3O^+$. It is simpler, however, to use $H_3O^+$ to represent the hydronium ion.




With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in $H_2O$:

$$HCl\,(g) + H_2O\,(\ell) \rightarrow H_3O^+\,(aq) + Cl^-\,(aq) \tag{11.3.2}$$

We can depict this process using Lewis electron dot diagrams:




Now we see that a hydrogen ion is transferred from the HCl molecule to the $H_2O$ molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; as a hydrogen ion acceptor, $H_2O$ is a Brønsted-Lowry base. So HCl is an acid not just in the Arrhenius sense, but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, $H_2O$ is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled $H_2O$ a base in this circumstance.

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.
- All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

### Example 11.3.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

**Solution**

$C_6H_5NH_2$ and $H_2O$ are the reactants. When $C_6H_5NH_2$ accepts a proton from $H_2O$, it gains an extra H and a positive charge and leaves an $OH^-$ ion behind. The reaction is as follows:

$$\mathbf{C_6H_5NH_2\,(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3^+\,(aq) + OH^-\,(aq)}$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The $H_2O$ molecule, because it donates a proton, is the Brønsted-Lowry acid.

### Exercise 11.3.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathbf{H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+}$$

**Answer**

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: $H_2O$

### Exercise 11.3.2

Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. $HPO_4^{2-}$
c. $H_3PO_4$
d. $NH_4^+$
e. $CH_3NH_3^+$

**Answer**

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an $H^+$. This eliminates $\mathbf{HCl}$, $\mathbf{H_3PO_4}$, $\mathbf{NH_4^+}$ and $\mathbf{CH_3NH_3^+}$ because they are Bronsted-Lowry acids. They all give away protons. In the case of $\mathbf{HPO_4^{2-}}$, consider the following equation:

$$\mathbf{HPO_4^{2-}\,(aq) + H_2O\,(l) \rightarrow PO_4^{3-}\,(aq) + H_3O^+\,(aq)}$$

Here, it is clear that $HPO_4^{2-}$ is the acid since it donates a proton to water to make $H_3O^+$ and $PO_4^{3-}$. Now consider the following equation:

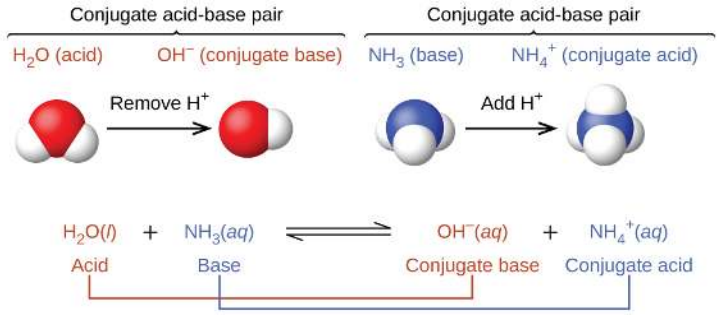
$$\mathbf{HPO_4^{2-}\,(aq) + H_2O\,(l) \rightarrow H_2PO_4^- + OH^-\,(aq)}$$

In this case, $HPO_4^{2-}$ is the base since it accepts a proton from water to form $H_2PO_4^-$ and $OH^-$. Thus, $HPO_4^{2-}$ is an acid and base together, making it amphoteric.

Since $HPO_4^{2-}$ is the only compound from the options that can act as a base, the answer is **(b) $\mathbf{HPO_4^{2-}}$.**

## Conjugate Acid-Base Pair

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, $\mathbf{OH^-}$, and the conjugate acid of ammonia, $\mathbf{NH_4^+}$:




This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O ( l ) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are $\boldsymbol{NH_4^+/NH_3}$ and $\boldsymbol{H_2O/OH^-}$.

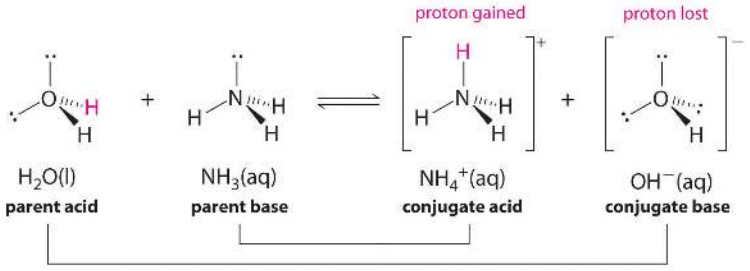



Figure 11.3.1. The pairing of parent acids and bases with conjugate acids and bases.


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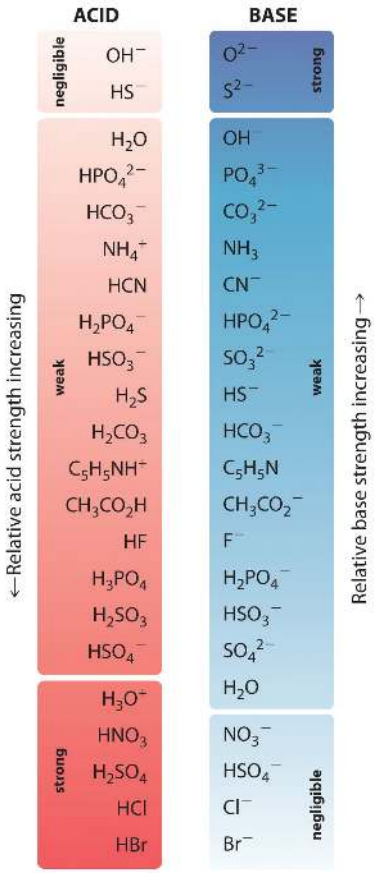



Figure 11.3.1: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

## Example 11.3.2

Identify the conjugate acid-base pairs in this equilibrium.

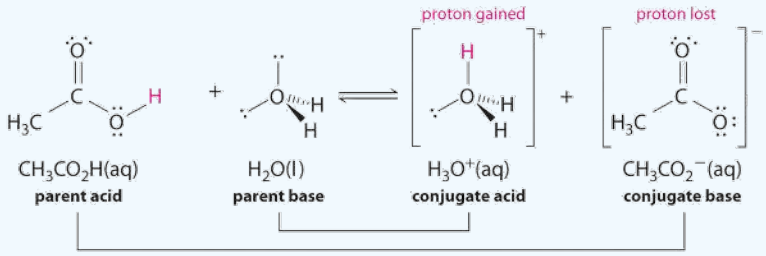
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

### Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, $\boldsymbol{H_3O^+}$ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($\boldsymbol{CH_3CO_2H/CH_3CO_2^-}$) and
- the parent base and its conjugate acid ($\boldsymbol{H_3O^+/H_2O}$).



**Example 11.3.3**

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

**Solution**

One pair is $H_2O$ and $OH^-$, where $H_2O$ has one more $H^+$ and is the conjugate acid, while $OH^-$ has one less $H^+$ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

**Exercise 11.3.3**

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

**Answer**

$H_2O$ (acid) and $OH^-$ (base); $NH_2^-$ (base) and $NH_3$ (acid)

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# 11.4: Reactions of Acids and Bases

**Learning Objectives**

- Write acid-base neutralization reactions.
- Write reactions of acids with metals.
- Write reactions of bases with metals.

## Neutralization Reactions

The reaction that happens when an acid, such as **HCl**, is mixed with a base, such as **NaOH**:

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

When an acid and a base are combined, water and a salt are the products. Salts are ionic compounds containing a positive ion other than $\mathrm{H^+}$ and a negative ion other than the hydroxide ion, $\mathrm{OH^-}$. Double displacement reactions of this type are called **neutralization reactions**. We can write an expanded version of this equation, with aqueous substances written in their longer form:

$$\mathrm{H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow Na^+\,(aq) + Cl^-\,(aq) + H_2O\,(l)}$$

After removing the spectator ions, we get the net ionic equation:

$$\mathrm{H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O\,(l)}$$

When a strong acid and a strong base are combined in the proper amounts—when $[\mathrm{H^+}]$ equals $[\mathrm{OH^-}]$\)—a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

Salt solutions do not always have a pH of 7, however. Through a process known as **hydrolysis**, the ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. As a general concept, if a strong acid is mixed with a weak base, the resulting solution will be slightly acidic. If a strong base is mixed with a weak acid, the solution will be slightly basic.



Video: Equimolar (~0.01 M) and equivolume solutions of **HCl** and **NaOH** are combined to make salt water. https://youtu.be/TS-I9KrUjB0

**Example 11.4.1: Propionic Acid + Calcium Hydroxide**

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($\mathrm{CH_3CH_2CO_2H}$) with aqueous calcium hydroxide [$\mathrm{Ca(OH)_2}$].

**Solution**

Solutions to Example 14.5.1

| Steps | Reaction |
|---|---|
| *Write the unbalanced equation.*<br>This is a double displacement reaction, so the cations and anions swap to create the water and the salt. | $CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + H_2O(l)$ |
| *Balance the equation.*<br>Because there are two $OH^-$ ions in the formula for $Ca(OH)_2$, we need two moles of propionic acid, $CH_3CH_2CO_2H$, to provide $H^+$ ions. | $\underline{2}CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + \underline{2}H_2O(l)$ |

**? Exercise 11.4.1**

Write a balanced chemical equation for the reaction of solid barium hydroxide with dilute acetic acid.

**Answer**

$$Ba(OH)_2\,(s) + 2\,CH_3CO_2H\,(aq) \longrightarrow Ba(CH_3CO_2)_2\,(aq) + 2\,H_2O\,(l)$$

## Acids and Bases React with Metals

Acids react with most metals to form a salt and hydrogen gas. As discussed previously, metals that are more active than acids can undergo a **single displacement reaction**. For example, zinc metal reacts with hydrochloric acid, producing zinc chloride and hydrogen gas.

$$Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

Bases also react with certain metals, like zinc or aluminum, to produce hydrogen gas. For example, sodium hydroxide reacts with zinc and water to form sodium zincate and hydrogen gas.

$$Zn\,(s) + 2\,NaOH\,(aq) + 2\,H_2O\,(l) \longrightarrow Na_2Zn(OH)_4\,(aq) + H_2\,(g).$$

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# 11.5: Strong and Weak Acids and Bases

**Learning Objectives**

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.
- Compare the strength of weak acids and bases using equilibrium concepts.

## Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider HCl(aq). When HCl is dissolved in $H_2O$, it completely dissociates into $H^+$(aq) and $Cl^-$(aq) ions; all the HCl molecules become ions:

$$HCl \xrightarrow{100\%} H^+(aq) + Cl^-(aq)$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq)$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

As it turns out, there are very few strong acids, which are given in Table **11.5.1**. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

> *Any acid that dissociates 100% into ions is called a strong acid. If it does not dissociate 100%, it is a weak acid.*

Table **11.5.1**: Strong Acids and Bases

| Acids | Bases |
|---|---|
| HCl | LiOH |
| HBr | NaOH |
| HI | KOH |
| $HNO_3$ | RbOH |
| $H_2SO_4$ | CsOH |
| $HClO_3$ | $Mg(OH)_2$ |
| $HClO_4$ | $Ca(OH)_2$ |
| | $Sr(OH)_2$ |
| | $Ba(OH)_2$ |

## Strong and Weak Bases

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (Table **11.5.1**); any base not listed is a weak base. All strong bases are $OH^-$ compounds. So a base based on some other mechanism, such as $NH_3$ (which does not contain $OH^-$ ions as part of its formula), will be a weak base.

### Example 11.5.1: Identifying Strong and Weak Acids and Bases

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. $C_5H_5N$

**Solution**

a. Because HCl is listed in Table **11.5.1**, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table **11.5.1**, it is a strong base.
c. The nitrogen in $C_5H_5N$ would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

### Exercise 11.5.1

Identify each acid or base as strong or weak.

a. **RbOH**
b. $\mathbf{HNO_2}$

**Answer a**

strong base

**Answer b**

weak acid

### Example 11.5.2: Characterizing Base Ionization

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

**Solution**

This is an ionic compound of $Ca^{2+}$ ions and $OH^-$ ions. When an ionic compound dissolves, it separates into its constituent ions:

$$\mathbf{Ca(OH)_2 \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)}$$

Because $Ca(OH)_2$ is listed in Table **11.5.1**, this reaction proceeds 100% to products.

### Exercise 11.5.2

Write the balanced chemical equation for the dissociation of hydrazoic acid ($HN_3$) and indicate whether it proceeds 100% to products or not.

**Answer a**

The reaction is as follows:

$$\mathbf{HN_3 \longrightarrow H^+(aq) + N_3^-(aq)}$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

## Chemical Equilibrium in Weak Acids and Bases

The behavior of **weak acids and bases** illustrates a key concept in chemistry. Does the chemical reaction describing the ionization of a weak acid or base just stop when the acid or base is done ionizing? Actually, no. Rather, the reverse process—the reformation

of the molecular form of the acid or base—occurs, ultimately at the same rate as the ionization process. For example, the ionization of the weak acid $\mathbf{HC_2H_3O_2\,(aq)}$ is as follows:

$$\mathbf{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{11.5.1}$$

The reverse process also begins to occur:

$$\mathbf{H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) + H_2O(\ell)} \tag{11.5.2}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$\mathbf{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{11.5.3}$$

The $\rightleftharpoons$ implies that **both the forward and reverse reactions** are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

### ✔ Example 11.5.3: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HNO_2$(aq)
b. $C_5H_5N$(aq)

**Solution**

a. $HNO_2(aq) + H_2O(\ell) \leftrightarrows NO_2^-(aq) + H_3O^+(aq)$
b. $C_5H_5N(aq) + H_2O(\ell) \leftrightarrows C_5H_5NH^+(aq) + OH^-(aq)$

### ? Exercise 11.5.3

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $\boldsymbol{HF_{(aq)}}$
b. $\boldsymbol{AgOH_{(aq)}}$
c. $CH_3NH_2$(aq)

**Answer**

a. $HF(aq) + H_2O(\ell) \leftrightarrows F^-(aq) + H_3O^+(aq)$

b. $AgOH(aq) \leftrightarrows Ag^+(aq) + OH^-(aq)$

c. $CH_3NH_2(aq) + H_2O(\ell) \leftrightarrows CH_3NH_3^+(aq) + OH^-(aq)$

## Acid Ionization Constant, $K_a$

The ionization for a general weak acid, **HA**, can be written as follows:

$$\mathbf{HA}\,(aq) \rightleftharpoons \mathbf{H^+}\,(aq) + \mathbf{A^-}\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** ($K_a$) is the equilibrium constant for the ionization of an acid.

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of $K_a$ is a reflection of the strength of the acid. Weak acids with relatively higher $K_a$ values are stronger than acids with relatively lower $K_a$ values. Because strong acids are essentially 100% ionized, the concentration of the acid in the denominator is nearly zero and the $K_a$ value approaches infinity. For this reason, $K_a$ values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table **11.5.1**: Acid Ionization Constants at **25°C**

| Name of Acid | Ionization Equation | $K_a$ |
|---|---|---|
| Sulfuric acid | $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$<br>$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ | very large<br>$1.3 \times 10^{-2}$ |
| Hydrofluoric acid | $HF \rightleftharpoons H^+ + F^-$ | $7.1 \times 10^{-4}$ |
| Nitrous acid | $HNO_2 \rightleftharpoons H^+ + NO_2^-$ | $4.5 \times 10^{-4}$ |
| Benzoic acid | $C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$ | $6.5 \times 10^{-5}$ |
| Acetic acid | $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ | $1.8 \times 10^{-5}$ |
| Carbonic acid | $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$<br>$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ | $4.2 \times 10^{-7}$<br>$4.8 \times 10^{-11}$ |

Hydrofluoric acid $HF_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

## Key Takeaways

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.
- Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.

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# 11.6: Water - Acid and Base in One

**Learning Objectives**

- Describe the autoionization of water.
- Calculate the concentrations of $H_3O^+$ and $OH^-$ in aqueous solutions, knowing the other concentration.

## Autoionozation of Water

We have already seen that $H_2O$ can act as an acid or a base:

$$\underbrace{NH_3}_{\text{base}} + \underbrace{H_2O}_{\text{acid}} \rightleftharpoons NH_4^+ + OH^-$$

where $H_2O$ acts as an acid (in red).

$$\underbrace{HCl}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \longrightarrow H_3O^+ + Cl^-$$

where $H_2O$ acts as an base (in blue).

It may not surprise you to learn, then, that within any given sample of water, some $H_2O$ molecules are acting as acids, and other $H_2O$ molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{11.6.1}$$

This occurs only to a very small degree: only about 6 in $10^8$ $H_2O$ molecules are participating in this process, which is called the **autoionization of water**.

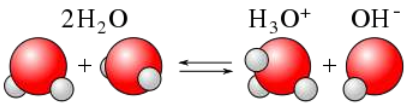



Figure 11.6.1: Autoionization of water, resulting in hydroxide and hydronium ions.

At this level, the concentration of both $H_3O^+(aq)$ and $OH^-(aq)$ in a sample of pure $H_2O$ is about $1.0 \times 10^{-7}\ M$ (at room temperature). If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \tag{11.6.2}$$

for *any* sample of pure water because H2O can act as both an acid and a base. The product of these two concentrations is $1.0 \times 10^{-14}$:

$$[H_3O^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of $H_3O^+(aq)$ (i.e., $[H_3O^+]$) is greater than $1.0 \times 10^{-7}\ M$.
- For bases the concentration of $OH^-(aq)$ (i.e., $[OH^-]$) is greater than $1.0 \times 10^{-7}\ M$.

However, the *product* of the two concentrations—$[H_3O^+][OH^-]$—is *always* equal to $1.0 \times 10^{-14}$, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted $K_w$:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{11.6.3}$$

This means that if you know $[H_3O^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal $1.0 \times 10^{-14}$; or if you know $[OH^-]$), you can calculate $[H_3O^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of $K_w$.

**Warning: Temperature Matters**

The degree of autoionization of water (Equation 11.6.1)—and hence the value of $K_w$—changes with temperature, so Equations 11.6.2 - 11.6.3 are accurate only at room temperature.

**Example 11.6.1: Hydroxide Concentration**

What is $[OH^-]$) of an aqueous solution if $[H_3O^+]$ is $1.0 \times 10^{-4} M$?

**Solution**

Solutions to Example 14.7.1

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: $[H_3O^+] = 1.0 \times 10^{-4}\ M$<br>Find: $[OH^-]$ = ? M |
| List other known quantities. | none |
| Plan the problem. | Using the expression for $K_w$, (Equation 11.6.3), rearrange the equation algebraically to solve for $[OH^-]$.<br>$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$$ |
| Calculate. | Now substitute the known quantities into the equation and solve.<br>$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$$<br>It is assumed that the concentration unit is molarity, so $[OH^-]$ is $1.0 \times 10^{-10}$ M. |
| Think about your result. | The concentration of the acid is high (> 1 x $10^{-7}$ M), so $[OH^-]$ should be low. |

**Exercise 11.6.1**

What is $[OH^-]$ in a 0.00032 M solution of $H_2SO_4$?

**Hint**

Assume **both** protons ionize from the molecule...although this is not the case.

**Answer**

$3.1 \times 10^{-11}\ M$

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of $H_3O^+$ or $OH^-$ ions in the formula unit because $[H_3O^+]$ or $[OH^-]$) may not be the same as the concentration of the acid or base itself.

**Example 11.6.2: Hydronium Concentration**

What is $[H_3O^+]$ in a 0.0044 M solution of $Ca(OH)_2$?

**Solution**

Solutions to Example 14.7.2

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: $[Ca(OH)_2] = 0.0044\,M$<br>Find: $[H_3O^+]$ = ? M |
| List other known quantities. | We begin by determining $[OH^-]$. The concentration of the solute is 0.0044 M, but because $Ca(OH)_2$ is a strong base, there are two $OH^-$ ions in solution for every formula unit dissolved, so the actual $[OH^-]$ is two times this:<br>$$[OH^-] = 2 \times 0.0044\ \text{M} = 0.0088\,\text{M}\cdot$$ |
| Plan the problem. | Use the expression for $K_w$ (Equation 11.6.3) and rearrange the equation algebraically to solve for $[H_3O^+]$.<br>$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$ |
| Calculate. | Now substitute the known quantities into the equation and solve.<br>$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12} M$$<br>$[H_3O^+]$ has decreased significantly in this basic solution. |
| Think about your result. | The concentration of the base is high (> 1 x $10^{-7}$ M) so Extra close brace or missing open brace should be low. |

**? Exercise 11.6.2**

What is $[H_3O^+]$ of an aqueous solution if $[OH^-]$ is $1.0 \times 10^{-9}\,M$?

**Answer**

$1.0 \times 10^{-5}$ M

In any aqueous solution, the product of $[H_3O^+]$ and $[OH^-]$ equals $1.0 \times 10^{-14}$ (at room temperature).

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# 11.7: The pH and pOH Scales - Ways to Express Acidity and Basicity

**Learning Objectives**

- Define pH and pOH.
- Determine the pH of acidic and basic solutions.
- Determine the hydronium ion concentration and pOH from pH.

## The pH Scale

As we have seen, $[H_3O^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

$pH$ is a logarithmic function of $[H_3O^+]$:

$$pH = -\log[H_3O^+] \tag{11.7.1}$$

$pH$ is usually (but not always) between 0 and 14. Knowing the dependence of $pH$ on $[H_3O^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the $pH$ scale. The pH scale is the range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use $pH$ to make a quick determination whether a given aqueous solution is acidic, basic, or neutral. Figure **11.7.1** illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative* log of** $[H_3O^+]$, which will give a positive value for pH.

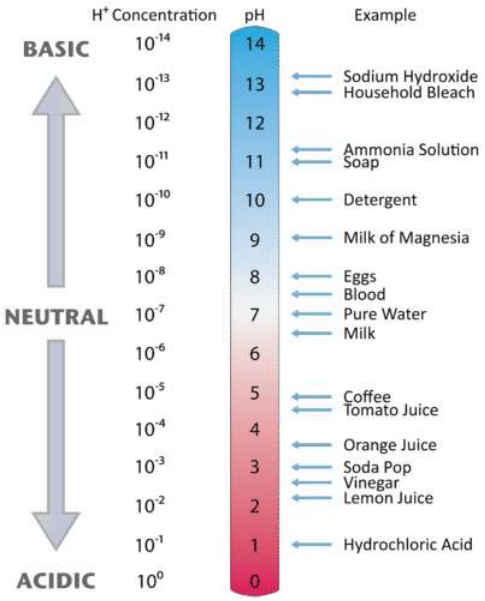



Figure **11.7.1**: The $pH$ values for several common materials.

**Example 11.7.1**

Label each solution as acidic, basic, or neutral based only on the stated $pH$.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

***Answer***

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

**? Exercise 11.7.1**

Identify each substance as acidic, basic, or neutral based only on the stated $pH$.

a. human blood with $pH$ = 7.4
b. household ammonia with $pH$ = 11.0
c. cherries with $pH$ = 3.6

**Answer a**

basic

**Answer b**

basic

**Answer c**

acidic

## Calculating pH from Hydronium Concentration

The pH of solutions can be determined by using logarithms as illustrated in the next example for stomach acid. Stomach acid is a solution of $HCl$ with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$, what is the $pH$ of the solution?

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

**Logarithms**

To get the **log value** on your calculator, enter the number (in this case, the hydronium ion concentration) first, then press the LOG key.

If the number is 1.0 x $10^{-5}$ (for $[H_3O^+]$ = 1.0 x $10^{-5}$ M) you should get an answer of "-5".

If you get a different answer, or an error, try pressing the LOG key before you enter the number.

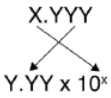
**Example 11.7.2: Converting Ph to Hydronium Concentration**

Find the pH, given the $[H_3O^+]$ of the following:

a. 1 ×$10^{-3}$ M
b. 2.5 ×$10^{-11}$ M
c. 4.7 ×$10^{-9}$ M

**Solution**

Solutions to Example 14.9.2

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>a. $[H_3O^+] = 1 \times 10^{-3}$ M<br>b. $[H_3O^+] = 2.5 \times 10^{-11}$ M<br>c. $[H_3O^+] = 4.7 \times 10^{-9}$ M<br>Find: ? pH |
| Plan the problem. | Need to use the expression for pH (Equation 11.7.1).<br>$pH = -\log [H_3O^+]$ |
| Calculate. | Now substitute the known quantity into the equation and solve.<br>a. $pH = -\log [1 \times 10^{-3}] = 3.0$ (1 decimal places since 1 has 1 significant figure)<br>b. $pH = -\log [2.5 \times 10^{-11}] = 10.60$ (2 decimal places since 2.5 has 2 significant figures)<br>c. $pH = -\log [4.7 \times 10^{-9}] = 8.30$ (2 decimal places since 4.7 has 2 significant figures)<br>The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer:<br>  |

## ? Exercise 11.7.2

Find the pH, given $[H_3O^+]$ of the following:

a. $5.8 \times 10^{-4}$ M
b. $1.0 \times 10^{-7}$

**Answer a**

3.22

**Answer b**

7.00

### Calculating Hydronium Concentration from pH

Sometimes you need to work "backwards"—you know the pH of a solution and need to find $[H_3O^+]$, or even the concentration of the acid solution. How do you do that? To convert pH into $[H_3O^+]$ we solve Equation 11.7.1 for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[H_3O^+] = \text{antilog}(-pH)$$

or

$$[H_3O^+] = 10^{-pH} \tag{11.7.2}$$

As mentioned above, different calculators work slightly differently—make sure you can do the following calculations using ***your*** calculator.

## Calculator Skills

We have a solution with a pH = 8.3. What is $[H_3O^+]$ ?

**With some calculators you will do things in the following order:**

1. Enter 8.3 as a negative number (use the key with both the +/- signs, not the subtraction key).
2. Use your calculator's 2nd or Shift or INV (inverse) key to type in the symbol found above the LOG key. The shifted function should be $10^x$.
3. You should get the answer $\mathbf{5.0 \times 10^{-9}}$.

**Other calculators require you to enter keys in the order they appear in the equation.**

1. Use the Shift or second function to key in the $10^x$ function.
2. Use the +/- key to type in a negative number, then type in 8.3.
3. You should get the answer $\mathbf{5.0 \times 10^{-9}}$.

If neither of these methods work, try rearranging the order in which you type in the keys. Don't give up—you must master your calculator!

## Example 11.7.3: Calculating Hydronium Concentration from pH

Find the hydronium ion concentration in a solution with a pH of 12.6. Is this solution an acid or a base? How do you know?

### Solution

Solutions to Example 14.9.3

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: pH = 12.6<br>Find: $[H_3O^+]$ = ? M |
| Plan the problem. | Need to use the expression for $[H_3O^+]$ (Equation 11.7.2).<br>$[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$ |
| Calculate. | Now substitute the known quantity into the equation and solve.<br>$[H_3O^+]$ = antilog (12.60) = 2.5 x $10^{-13}$ M (2 significant figures since 4.7 has 12.60 2 decimal places)<br>or<br>$[H_3O^+] = 10^{-12.60} = 2.5 \times 10^{-13}$ M (2 significant figures since 4.7 has 12.60 2 decimal places)<br>The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer:<br>X.YYY<br>Y.YY x $10^x$ |

## Exercise 11.7.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

**Answer**

1.5 x $10^{-8}$ M

## The pOH scale

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration.

$$\mathrm{pOH} = -\log\left[\mathrm{OH}^-\right]$$

The relation between the hydronium and hydroxide ion concentrations expressed as p-functions is easily derived from the $K_w$ expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH}^-] \tag{11.7.3}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH}^-]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH}^-] \tag{11.7.4}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{11.7.5}$$

At 25 °C, the value of $K_w$ is $1.0 \times 10^{-14}$, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{11.7.6}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{11.7.7}$$

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{11.7.8}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

### Example 11.7.4:

Find the pOH of a solution with a pH of 4.42.

**Solution**

Solutions to Example 14.9.4

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: pH =4.42<br>Find: ? pOH |
| Plan the problem. | Need to use the expression<br>pOH = 14 - pH |
| Calculate. | Now substitute the known quantity into the equation and solve.<br>pOH=14−4.42=9.58 |
| Think about your result. | The pH is that of an acidic solution, and the resulting pOH is the difference after subtracting from 14. The answer has two significant figures because the given pH has two decimal places. |

### Exercise 11.7.4

The pH of a solution is 8.22. What is the pOH?

**Answer**

5.78

The diagram below shows all of the interrelationships between [H3O+][H3O+], [OH−][OH−], pH, and pOH.

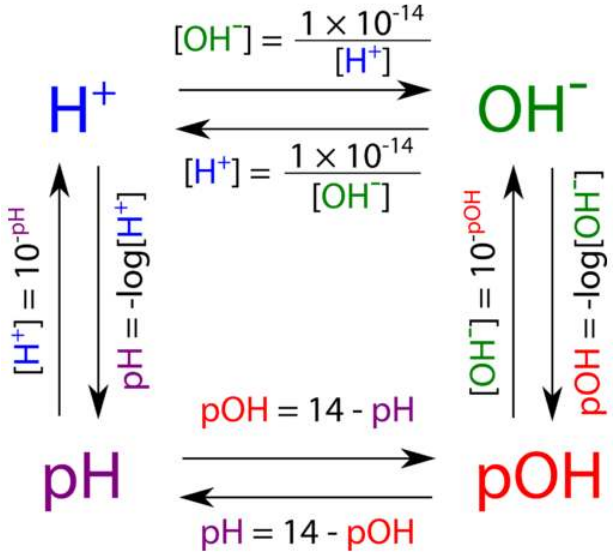



Figure **11.7.1**: Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH.

## Contributions & Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
-
- Template:OpenStax

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# 11.8: Buffer Solutions

**Learning Objectives**

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 11.8.1). A solution of acetic acid ($CH_3COOH$ and sodium acetate $CH_3COONa$) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ($NH_3\,(aq)$) and ammonium chloride ( $NH_4Cl\,(aq)$).




Figure 11.8.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

## How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the $K_a$ of acetic acid is greater than the $K_b$ of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2{}^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 11.8.2).

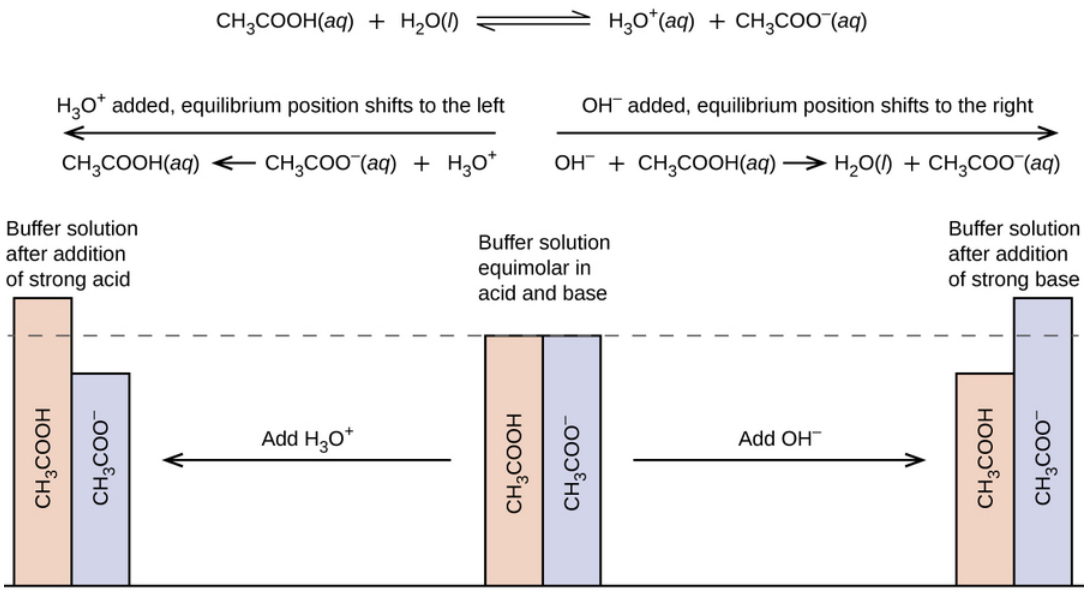



Figure **11.8.2**: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the $K_b$ for ammonia is greater than the $K_a$ for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathbf{NH_4^+}(aq) + \mathbf{OH^-}(aq) \longrightarrow \mathbf{NH_3}(aq) + \mathbf{H_2O}(l)$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathbf{H_3O^+}(aq) + \mathbf{NH_3}(aq) \longrightarrow \mathbf{NH_4^+}(aq) + \mathbf{H_2O}(l)$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

### Example 11.8.1: pH Changes in Buffered and Unbuffered Solutions

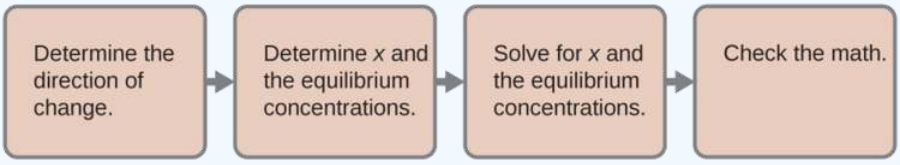
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

**Solution**

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):




1. *Determine the direction of change.* The equilibrium in a mixture of $H_3O^+$, $\mathbf{CH_3CO_2^-}$, and $CH_3CO_2H$ is:

$$\mathbf{CH_3CO_2H}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{CH_3CO_2^-}(aq)$$

The equilibrium constant for $CH_3CO_2H$ is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[CH_3CO_2H] = [CH_3CO_2^-] = 0.10\ M$ and $[H_3O^+] = \sim 0\ M$, the reaction shifts to the right to form $H_3O^+$.

2. *Determine* x *and equilibrium concentrations*. A table of changes and concentrations follows:

| | $[CH_3CO_2H] + [H_2O] \rightleftharpoons H_3O^+ + [CH_3CO_2^-]$ | | |
|---|---|---|---|
| Initial concentration (*M*) | 0.10 | ~0 | 0.10 |
| Change (*M*) | $-x$ | $x$ | $x$ |
| Equilibrium constant (*M*) | $0.10 - x$ | $x$ | $0.10 + x$ |

- *Solve for x and the equilibrium concentrations.* We find:

$$x = 1.8 \times 10^{-5}\ M$$

- and

$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5}\ M$$

Thus:

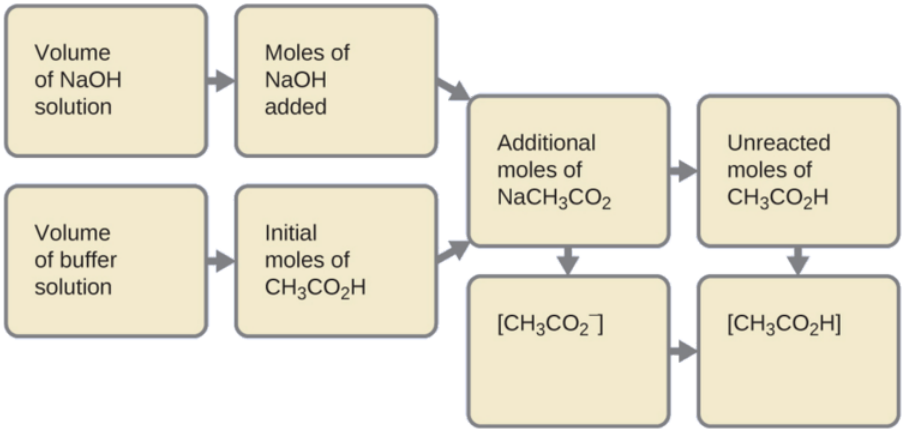
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

4. *Check the work*. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:




1. *Determine the moles of NaOH*. One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

$$0.0010\,\cancel{L} \times \left(\frac{0.10\ \text{mol NaOH}}{1\,\cancel{L}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH}$$

2. *Determine the moles of $CH_2CO_2H$*. Before reaction, 0.100 L of the buffer solution contains:

$$0.100\,\cancel{L} \times \left(\frac{0.100\ \text{mol } CH_3CO_2H}{1\,\cancel{L}}\right) = 1.00 \times 10^{-2}\ \text{mol } CH_3CO_2H$$

3. *Solve for the amount of $NaCH_3CO_2$ produced.* The $1.0 \times 10^{-4}$ mol of NaOH neutralizes $1.0 \times 10^{-4}$ mol of $CH_3CO_2H$, leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

and producing $1.0 \times 10^{-4}$ mol of $NaCH_3CO_2$. This makes a total of:

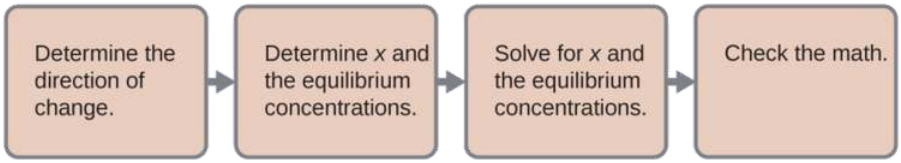
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \nonumber \]

4. *Find the molarity of the products.* After reaction, $CH_3CO_2H$ and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098\ M$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100\ M$$

Now we calculate the pH after the intermediate solution, which is 0.098 *M* in $CH_3CO_2H$ and 0.100 *M* in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:




*This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.*

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a $1.8 \times 10^{-5}$-*M* solution of HCl). The volume of the final solution is 101 mL.

**Solution**

This $1.8 \times 10^{-5}$-*M* solution of HCl has the same hydronium ion concentration as the 0.10-*M* solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100 \text{ L} \times \left( \frac{1.8 \times 10^{-5} \text{ mol HCl}}{1 \text{ L}} \right) = 1.8 \times 10^{-6} \text{ mol HCl}$$

As shown in part (b), 1 mL of 0.10 *M* NaOH contains $1.0 \times 10^{-4}$ mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5}\ M$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5}\ M \text{ NaOH}}{0.101 \text{ L}} = 9.7 \times 10^{-4}\ M$$

The pOH of this solution is:

$$\text{pOH} = -\log[OH^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

**? Exercise 11.8.1**

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a $1.8 \times 10^{-5}$ *M* HCl solution from 4.74 to 3.00.

**Answer**

Initial pH of $1.8 \times 10^{-5}$ *M* HCl; pH = $-\log[H_3O^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of $H_3O^+$ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L × 0.0010 L = $1.0 \times 10^{-4}$ moles; final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right) = 3.00$$

## Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure **11.8.3**). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.



Figure **11.8.3**: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

## Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure **11.8.4** shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

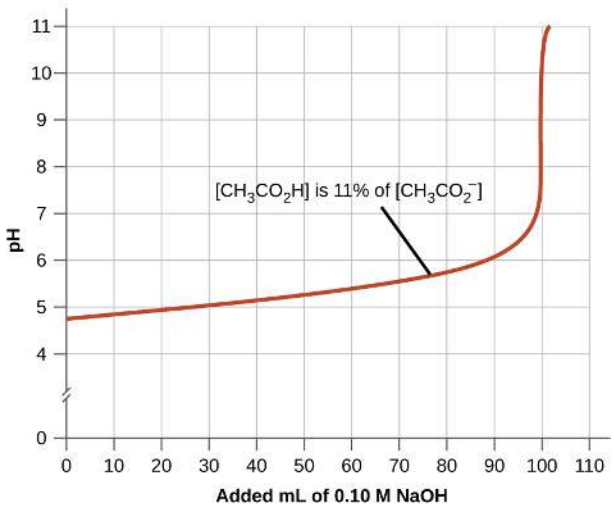



Figure **11.8.4**: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2^-] = 0.10\ M$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, $H_2CO_3$, and the bicarbonate ion, $HCO_3^-$. When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

## The Henderson-Hasselbalch Approximation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

Rearranging to solve for $[H_3O^+]$, we get:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

which can be written as

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

where $pK_a$ is the negative of the common logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch approximation, to calculate the pH of buffer solutions. It is important to note that the "$x$ is small" assumption must be valid to use this equation.

## Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

## Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{H_3O^+}(aq)$$

The concentration of carbonic acid, $H_2CO_3$ is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathbf{HCO_3^-}$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the p$K_a$ of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the $H_2CO_3$ concentration is significantly lower than that of the $\mathbf{HCO_3^-}$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathbf{HCO_3^-}$ ion, producing $H_2CO_3$. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes $CO_2$ from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases $CO_2$ concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

## Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

## Key Equations

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$
- $\mathrm{pH} = pK_a + \log \frac{[A^-]}{[HA]}$

## Glossary

**buffer capacity**

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

**buffer**

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

**Henderson-Hasselbalch equation**

equation used to calculate the pH of buffer solutions

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# 11.9: Acid–Base Titration

**Learning Objectives**

- Understand the basics of acid-base titrations.
- Understand the use of indicators.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because so many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

During an acid-base titration, an acid with a known concentration (a **standard solution**) is slowly added to a base with an unknown concentration (or vice versa). A few drops of indicator solution are added to the base. The indicator will signal, by color change, when the base has been neutralized (when $[H^+] = [OH^-]$). At that point—called the **equivalence point,** or **end point**—the titration is stopped. By knowing the volumes of acid and base used, and the concentration of the standard solution, calculations allow us to determine the concentration of the other solution.

It is important to accurately measure volumes when doing titrations. The instrument you would use is called a burette (or buret).



Figure **11.9.1**: Equipment for Titrations. A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed.

For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

$$\text{\# mol HCl} = (0.02566\ \text{L})(0.1078\ \text{M}) = 0.002766\ \text{mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$\mathrm{HCl + NaOH \longrightarrow NaCl + H_2O}$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766\ \cancel{mol\ HCl} \times \frac{1\ mol\ NaOH}{1\ \cancel{mol\ HCl}} = 0.002766\ mol\ NaOH$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766\ \cancel{mol\ HCl} \times \frac{40.00\ g\ NaOH}{1\ \cancel{mol\ HCl}} = 0.1106\ g\ NaOH$$

This type of calculation is performed as part of a titration.

**Example 11.9.1: Equivalence Point**

What mass of $Ca(OH)_2$ is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M $HNO_3$? The balanced chemical equation is as follows:

$$\mathrm{2\,HNO_3 + Ca(OH)_2 \longrightarrow Ca(NO_3)_2 + 2\,H_2O}$$

**Solution**

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

# moles $HNO_3$ = (0.04402 L)(0.0885 M) = 0.00390 mol $HNO_3$

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390\ \cancel{mol\ HNO_3} \times \frac{1\ mol\ Ca(OH)_2}{2\ \cancel{mol\ HNO_3}} = 0.00195\ mol\ Ca(OH)_2$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195\ \cancel{mol\ Ca(OH)_2} \times \frac{74.1\ g\ Ca(OH)_2}{\cancel{mol\ Ca(OH)_2}} = 0.144\ g\ Ca(OH)_2$$

**? Exercise 11.9.1**

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$H_2C_2O_4 + 2\,NaOH \longrightarrow Na_2C_2O_4 + 2\,H_2O$$

**Answer**

0.182 g

**? Exercise 11.9.2**

If 25.00 mL of HCl solution with a concentration of 0.1234 M is neutralized by 23.45 mL of NaOH, what is the concentration of the base?

**Answer**

0.1316 M NaOH

**? Exercise 11.9.3**

A 20.0 mL solution of strontium hydroxide, $Sr(OH)_2$, is placed in a flask and a drop of indicator is added. The solution turns color after 25.0 mL of a standard 0.0500 M HCl solution is added. What was the original concentration of the $Sr(OH)_2$ solution?

**Answer**

$3.12 \times 10^{-2}\ M$ $Sr(OH)_2$

## Indicator Selection for Titrations

The indicator used depends on the type of titration performed. The indicator of choice should change color when enough of one substance (acid or base) has been added to exactly use up the other substance. Only when a strong acid and a strong base are produced will the resulting solution be neutral. The three main types of acid-base titrations, and suggested indicators, are:

The three main types of acid-base titrations, suggested indicators, and explanations

| Titration between . . . | Indicator | Explanation |
|---|---|---|
| strong acid and strong base | any | |
| strong acid and weak base | methyl orange | changes color in the acidic range (3.2 - 4.4) |
| weak acid and strong base | phenolphthalein | changes color in the basic range (8.2 - 10.6) |

## Summary

A titration is the quantitative reaction of an acid and a base. Indicators are used to show that all the analyte has reacted with the titrant.

## Contributions & Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

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# CHAPTER OVERVIEW

## 12: Nuclear Chemistry

In today's society, the term *radioactivity* conjures up a variety of images:

- Nuclear power plants producing hydrocarbon-free energy, but with potentially deadly by-products that are difficult to store safely.
- Bombs with the capacity to use nuclear reactions that produce devastating explosions with horrible side effects on the earth as we know it, and on the surviving populations that inhabit it.
- Medical technology that utilizes nuclear chemistry to peer inside living things to detect disease, and the power to irradiate tissues to potentially cure these diseases.
- Fusion reactors that hold the promise of limitless energy with few toxic side products.

Radioactivity has a colorful history and clearly presents a variety of social and scientific dilemmas. In this chapter we will introduce the basic concepts of radioactivity, nuclear equations, and the processes involved in nuclear fission and nuclear fusion.


12.1: The Discovery of Radioactivity

12.2: Types of Radioactivity- Alpha, Beta, and Gamma Decay

12.3: Natural Radioactivity and Half-Life

12.3.1: Radiocarbon Dating- Using Radioactivity to Measure the Age of Fossils and Other Artifacts

12.4: The Discovery of Fission and the Atomic Bomb

12.5: Nuclear Power

12.6: Biological Effect and Application of Radiation


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# 12.1: 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 **12.1.1**: 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 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.

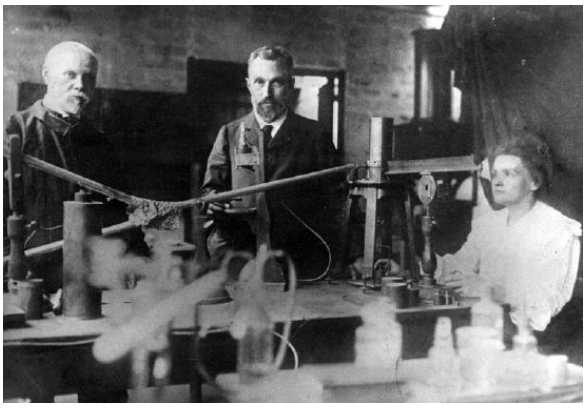


Figure 12.1.2: Marie Curie (right) and Pierre Curie (middle) with Henri Becquerel (left) shared the 1903 Nobel Prize.

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, $\alpha$, was a helium nucleus (a particle containing two protons and two neutrons), a beta particle, $\beta$, was a high speed electron, and gamma rays, $\gamma$, 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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https://chem.libretexts.org/@go/page/393950

# 12.2: Types of Radioactivity- Alpha, Beta, and Gamma Decay

**Learning Objectives**

- Compare qualitatively the ionizing and penetration power of alpha particles ($\alpha$), beta particles ($\beta$), and gamma rays ($\gamma$).
- Express the changes in the atomic number and mass number of a radioactive nuclei when an alpha, beta, or gamma particle is emitted.
- Write nuclear equations for alpha and beta decay reactions.

Many nuclei are radioactive; that is, they decompose by emitting particles and in doing so, become a different nucleus. In our studies up to this point, atoms of one element were unable to change into different elements. That is because in all other types of changes discussed, only the electrons were changing. In these changes, the nucleus, which contains the protons that dictate which element an atom is, is changing. All nuclei with 84 or more protons are radioactive, and elements with less than 84 protons have both stable and unstable isotopes. All of these elements can go through nuclear changes and turn into different elements.

In natural radioactive decay, three common emissions occur. When these emissions were originally observed, scientists were unable to identify them as some already known particles and so named them:

- alpha particles ($\alpha$)
- beta particles ($\beta$)
- gamma rays ($\gamma$)

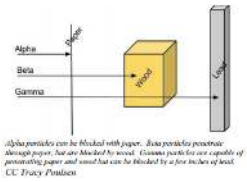
These particles were named using the first three letters of the Greek alphabet. Some later time, alpha particles were identified as helium-4 nuclei, beta particles were identified as electrons, and gamma rays as a form of electromagnetic radiation like x-rays, except much higher in energy and even more dangerous to living systems.

## The Ionizing and Penetration Power of Radiation

With all the radiation from natural and man-made sources, we should quite reasonably be concerned about how all the radiation might affect our health. The damage to living systems is done by radioactive emissions when the particles or rays strike tissue, cells, or molecules and alter them. These interactions can alter molecular structure and function; cells no longer carry out their proper function and molecules, such as DNA, no longer carry the appropriate information. Large amounts of radiation are very dangerous, even deadly. In most cases, radiation will damage a single (or very small number) of cells by breaking the cell wall or otherwise preventing a cell from reproducing.

The ability of radiation to damage molecules is analyzed in terms of what is called **ionizing power**. When a radiation particle interacts with atoms, the interaction can cause the atom to lose electrons and thus become ionized. The greater the likelihood that damage will occur by an interaction is the ionizing power of the radiation.

Much of the threat from radiation is involved with the ease or difficulty of protecting oneself from the particles. How thick of a wall do you need to hide behind to be safe? The ability of each type of radiation to pass through matter is expressed in terms of **penetration power.** The more material the radiation can pass through, the greater the penetration power and the more dangerous it is. In general, the greater mass present, the greater the ionizing power, and the lower the penetration power.



Alpha particles can be blocked with paper. Beta particles penetrate through paper, but are blocked by wood. Gamma particles are capable of penetrating paper and wood but can be blocked by a few inches of lead. CC Tracy Poulsen

Comparing only the three common types of ionizing radiation, alpha particles have the greatest mass. Alpha particles have approximately four times the mass of a proton or neutron and approximately 8,000 times the mass of a beta particle. Because of the large mass of the alpha particle, it has the highest ionizing power and the greatest ability to damage tissue. That same large size of alpha particles, however, makes them less able to penetrate matter. They collide with molecules very quickly when striking matter, add two electrons, and become a harmless helium atom. Alpha particles have the least penetration power and can be stopped by a thick sheet of paper or even a layer of clothes. They are also stopped by the outer layer of dead skin on people. This may seem to remove the threat from alpha particles, but it is only from external sources. In a nuclear explosion or some sort of nuclear accident, where radioactive emitters are spread around in the environment, the emitters can be inhaled or taken in with food or water and once the alpha emitter is inside you, you have no protection at all.

Beta particles are much smaller than alpha particles and therefore, have much less ionizing power (less ability to damage tissue), but their small size gives them much greater penetration power. Most resources say that beta particles can be stopped by a one-quarter inch thick sheet of aluminum. Once again, however, the greatest danger occurs when the beta emitting source gets inside of you.

Gamma rays are not particles, but a high energy form of electromagnetic radiation (like x-rays, except more powerful). Gamma rays are energy that has no mass or charge. Gamma rays have tremendous penetration power and require several inches of dense material (like lead) to shield them. Gamma rays may pass all the way through a human body without striking anything. They are considered to have the least ionizing power and the greatest penetration power.

Table **12.2.1** Comparison of Penetrating Power,Ionizing Power and Shielding of Alpha and Beta Particles, and Gamma Rays.

| Particle | Symbol | Mass | Penetrating Power | Ionizing Power | Shielding |
|---|---|---|---|---|---|
| Alpha | $\alpha$ | 4amu | Very Low | Very High | Paper Skin |
| Beta | $\beta$ | 1/2000amu | Intermediate | Intermediate | Aluminum |
| Gamma | $\gamma$ | 0 (energy only) | Very High | Very Low | 2 inches lead |

The safest amount of radiation to the human body is zero. It is impossible to completely avoid ionizing radiation, so the next best goal is to be exposed to as little as possible. The two best ways to minimize exposure are to limit time of exposure, and to increase distance from the source.

### Alpha Decay

The nuclear disintegration process that emits alpha particles is called alpha decay. An example of a nucleus that undergoes alpha decay is uranium-238. The alpha decay of U-238 is

$$^{238}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th} \tag{12.2.1}$$

In this nuclear change, the uranium atom ($^{238}_{92}\text{U}$) transmuted into an atom of thorium ($^{234}_{90}\text{Th}$) and, in the process, gave off an alpha particle. Look at the symbol for the alpha particle: $^{4}_{2}\text{He}$. Where does an alpha particle get this symbol? The bottom number in a nuclear symbol is the number of protons. That means that the alpha particle has two protons in it that were lost by the uranium atom. The two protons also have a charge of +2. The top number, 4, is the mass number or the total of the protons and neutrons in the particle. Because it has two protons, and a total of four protons and neutrons, alpha particles must also have two neutrons. Alpha particles always have this same composition: two protons and two neutrons.

Another alpha particle producer is thorium-230.

$$^{230}_{90}\text{Th} \rightarrow {}^{4}_{2}\text{He} + {}^{226}_{88}\text{Ra} \tag{12.2.2}$$

These types of equations are called nuclear equations and are similar to the chemical equivalent discussed through the previous chapters.

### Beta Decay

Another common decay process is beta particle emission, or beta decay. A beta particle is simply a high energy electron that is emitted from the nucleus. It may occur to you that we have a logically difficult situation here. Nuclei do not contain electrons and yet during beta decay, an electron is emitted from a nucleus. At the same time that the electron is being ejected from the nucleus, a neutron is becoming a proton. It is tempting to picture this as a neutron breaking into two pieces with the pieces being a proton and an electron. That would be convenient for simplicity, but unfortunately that is not what happens (more on this subject will be explained at the end of this section). For convenience, we will treat beta decay as a neutron splitting into a proton and an electron. The proton stays in the nucleus, increasing the atomic number of the atom by one. The electron is ejected from the nucleus and is the particle of radiation called beta.

To insert an electron into a nuclear equation and have the numbers add up properly, an atomic number and a mass number had to be assigned to an electron. The mass number assigned to an electron is zero (0), which is reasonable since the mass number is the number of protons plus neutrons, and an electron contains no protons and no neutrons. The atomic number assigned to an electron is negative one (-1), because that allows a nuclear equation containing an electron to balance atomic numbers. Therefore, the nuclear symbol representing an electron (beta particle) is

$$ {}^{0}_{-1}\text{e} \text{ or } {}^{0}_{-1}\beta $$

Thorium-234 is a nucleus that undergoes beta decay. Here is the nuclear equation for this beta decay:

$$ {}^{234}_{90}\text{Th} \rightarrow {}^{0}_{-1}\text{e} + {}^{234}_{91}\text{Pa} \tag{12.2.3} $$

## Gamma Radiation

Frequently, gamma ray production accompanies nuclear reactions of all types. In the alpha decay of $\text{U}$-238, two gamma rays of different energies are emitted in addition to the alpha particle.

$$ {}^{238}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th} + 2{}^{0}_{0}\gamma $$

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown. Nuclear reactions produce a great deal more energy than chemical reactions. Chemical reactions release the difference between the chemical bond energy of the reactants and products, and the energies released have an order of magnitude of $1 \times 10^{3}\ \text{kJ/mol}$. Nuclear reactions release some of the binding energy and may convert tiny amounts of matter into energy. The energy released in a nuclear reaction has an order of magnitude of $1 \times 10^{18}\ \text{kJ/mol}$. That means that nuclear changes involve almost **one million times more energy** per atom than chemical changes!

**Note**

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown.

The essential features of each reaction are shown in Figure 17.3.2

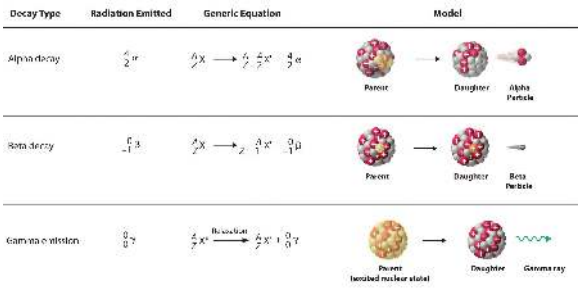



***Figure 17.3.2**: Three most common modes of nuclear decay.*

## "Nuclear Accounting"

When writing nuclear equations, there are some general rules that will help you:

- The sum of the mass numbers (top numbers) on the reactant side equal the sum of the mass numbers on the product side.
- The atomic numbers (bottom numbers) on the two sides of the reaction will also be equal.

In the alpha decay of ${}^{238}\text{U}$ (Equation 12.2.1), both atomic and mass numbers are conserved:

- mass number: $238 = 4 + 234$
- atomic number: $92 = 2 + 90$

Confirm that this equation is correctly balanced by adding up the reactants' and products' atomic and mass numbers. Also, note that because this was an alpha reaction, one of the products is the alpha particle, ${}^{4}_{2}\text{He}$.

Note that both the mass numbers and the atomic numbers add up properly for the beta decay of thorium-234 (Equation 12.2.3):

- mass number: $234 = 0 + 234$
- atomic number: $90 = -1 + 91$

The mass numbers of the original nucleus and the new nucleus are the same because a neutron has been lost, but a proton has been gained, and so the sum of protons plus neutrons remains the same. The atomic number in the process has been increased by one since the new nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has become a protactinium-234 nucleus. Protactinium-234 is also a beta emitter and produces uranium-234.

$$ {}^{234}_{91}\text{Pa} \rightarrow {}^{0}_{-1}\text{e} + {}^{234}_{92}\text{U} \tag{12.2.4} $$

Once again, the atomic number increases by one and the mass number remains the same; this confirms that the equation is correctly balanced.

**What About Balancing Charge?**

Both alpha and beta particles are charged, but nuclear reactions in Equations 12.2.1, 12.2.3, and most of the other nuclear reactions above, are not balanced with respect to charge, as discussed when balancing redox reactions. When studying nuclear reactions in general, there is typically little information or concern about the chemical state of the radioactive isotopes, because the electrons from the electron cloud are not directly involved in the nuclear reaction (in contrast to chemical reactions).

So it is acceptable to **ignore** charge in balancing nuclear reactions, and concentrate on balancing mass and atomic numbers only.

**Example 12.2.1**

Complete the following nuclear reaction by filling in the missing particle.

$$ {}^{210}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + ? $$

**Solution**

This reaction is an alpha decay. We can solve this problem one of two ways:

*Solution 1:* When an atom gives off an alpha particle, its atomic number drops by 2 and its mass number drops by 4, leaving: ${}^{206}_{84}\text{Po}$. We know the symbol is $\text{Po}$, for polonium, because this is the element with 84 protons on the periodic table.

*Solution 2:* Remember that the mass numbers on each side must total up to the same amount. The same is true of the atomic numbers.

- Mass numbers: $210 = 4 + ?$
- Atomic numbers: $86 = 2 + ?$

We are left with $^{206}_{84}\text{Po}$.

**Example 12.2.2**

Write each of the following nuclear reactions.

a) Carbon-14, used in carbon dating, decays by beta emission.

b) Uranium-238 decays by alpha emission.

**Solution**

a) Beta particles have the symbol $^{0}_{-1}\text{e}$. Emitting a beta particle causes the atomic number to increase by 1 and the mass number to not change. We get atomic numbers and symbols for elements using our periodic table. We are left with the following reaction:

$$^{14}_{6}\text{C} \rightarrow {}^{0}_{-1}\text{e} + {}^{14}_{7}\text{N}$$

b) Alpha particles have the symbol $^{4}_{2}\text{He}$. Emitting an alpha particle causes the atomic number to decrease by 2 and the mass number to decrease by 4. We are left with:

$$^{238}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th}$$

## Decay Series

The decay of a radioactive nucleus is a move toward becoming stable. Often, a radioactive nucleus cannot reach a stable state through a single decay. In such cases, a series of decays will occur until a stable nucleus is formed. The decay of **U**-238 is an example of this. The **U**-238 decay series starts with **U**-238 and goes through fourteen separate decays to finally reach a stable nucleus, **Pb**-206 (Figure 17.3.3). There are similar decay series for **U**-235 and **Th**-232. The **U**-235 series ends with **Pb**-207 and the **Th**-232 series ends with **Pb**-208.

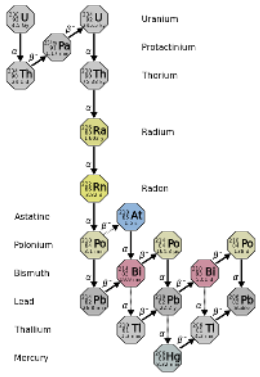



Figure 17.3.3: Uranium-238 decay chain. (CC-BY-3.0 Tosaka)

Several of the radioactive nuclei that are found in nature are present there because they are produced in one of the radioactive decay series. For example, there may have been radon on the earth at the time of its formation, but that original radon would have all decayed by this time. The radon that is present now is present because it was formed in a decay series (mostly by U-238).

## Summary

A nuclear reaction is one that changes the structure of the nucleus of an atom. The atomic numbers and mass numbers in a nuclear equation must be balanced. Protons and neutrons are made up of quarks. The two most common modes of natural radioactivity are alpha decay and beta decay. Most nuclear reactions emit energy in the form of gamma rays.

## Vocabulary

- **Alpha decay** - A common mode of radioactive decay in which a nucleus emits an alpha particle (a helium-4 nucleus).
- **Beta decay** - A common mode of radioactive decay in which a nucleus emits beta particles. The daughter nucleus will have a higher atomic number than the original nucleus.
- **Quark** - Particles that form one of the two basic constituents of matter. Various species of quarks combine in specific ways to form protons and neutrons, in each case taking exactly three quarks to make the composite particle.

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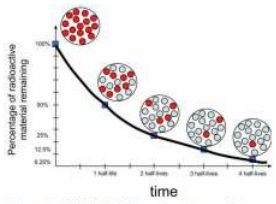
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# 12.3: Natural Radioactivity and Half-Life

**Learning Objectives**

- Describe what is meant by the term half-life and what factors affect half-life.
- Calculate the amount of radioactive material that will remain after an integral number of half-lives.
- Find the half-life of an isotope given graphical or other data.
- Describe how carbon-14 is used to determine the age of carbon-containing objects.

## Rate of Radioactive Decay



*After one half-life, half of the radioactive atoms have decayed. After another half-life, half of the remaining atoms have changed. This pattern continues, with half of the atoms changing over each half-life time.*
*CC Tracy Poulsen*

During natural radioactive decay, not all atoms of an element are instantaneously changed to atoms of another element. The decay process takes time and there is value in being able to express the rate at which a process occurs. A useful concept is **half-life**, which is the time required for half of the starting material to change or decay. Half-lives can be calculated from measurements on the change in mass of a nuclide and the time it takes to occur. The only thing we know is that in the time of that substance's half-life, half of the original nuclei will disintegrate. Although chemical changes are sped up or slowed down by changing factors such as temperature and concentration, these factors have no effect on half-life. Each radioactive isotope will have its own unique half-life that is independent of any of these factors.

The half-lives of many radioactive isotopes have been determined; they have been found to range from extremely long half-lives of 10 billion years, to extremely short half-lives of fractions of a second.

Table 17.5.1: Table of Selected Half-lives

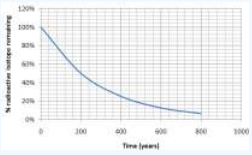
| Element | Mass Number (A) | Half-life | Element | Mass Number (A) | Half Life |
|---|---|---|---|---|---|
| Uranium | 238 | 4.5 Billion years | Californium | 251 | 800 years |
| Neptunium | 240 | 1 hour | Nobelium | 254 | 3 seconds |
| Plutonium | 243 | 5 hours | Carbon | 14 | 5730 years |
| Americium | 245 | 25 minutes | Carbon | 16 | 740 milliseconds |

The quantity of radioactive nuclei at any given time will decrease to half as much in one half-life. For example, if there are $100\ g$ of $Cf$-251 in a sample at some time, after 800 years, there will be $50\ g$ of $Cf$-251 remaining; after another 800 years (1600 years total), there will only be $25\ g$ remaining.

Remember, the half-life is the time it takes for half of your sample—no matter how much you have—to remain. Each half-life will follow the same general pattern as $Cf$-251. The only difference is the length of time it takes for half of a sample to decay.

**Example 12.3.3**

What is the half-life of an isotope that produces the following graph of decay over time?



**Solution**

We know that the half-life is the time it takes for half of a sample to change. How long did it take for half of our isotope to change? It took approximately 200 years for $100\%$ of our sample to leave only $50\%$ (half of the original amount) remaining. **The half-life is 200 years.**

*Notice that after another 200 years (400 years total), $25\%$ remains (half of $50\%$).

Look carefully at the graph in the previous example. All types of radioactive decay make a graph of the same general shape. The only difference is the scale and units of the $x$-axis, as the half-life time will be different.

**Example 12.3.2**

If there are 60 grams of Np-240 present, how much Np-240 will remain after 4 hours? (Np-240 has a half-life of 1 hour.)

**Solution**

We create a table based on Np-240's half-life of 1 hour.

| Amount of Np-240 present | Amount of time passed |
|---|---|
| 60 g | 0 (this is the amount before any time has passed) |
| 30 g | 1 hour (1 half-life) |
| 15 g | 2 hours (2 half-lives) |
| 7.5 g | 3 hours |
| 3.75 g | 4 hours |

After 4 hours, only 3.75 g of our original 60 g sample would remain of the radioactive isotope Np-240.

**Example 12.3.3**

A sample of Ac-225 originally contained 80 grams, and after 50 days only 2.55 grams of the original Ac-225 remain. What is the half life of Ac-225?

**Solution**

We will tackle this problem similarly to the last problem. The difference is that we are looking for the half-life time. Let's set up a similar table, though:

| Amount of Ac-225 present | Amount of time passed |
|---|---|
| 80 g | 0 |
| 40 g | 1 half-life |
| 20 g | 2 half-lives |
| 10 g | 3 half-lives |
| 5 g | 4 half-lives |
| 2.5 g | 5 half-lives |

We know that 50 days is the same as 5 half-lives. Therefore, 1 half-life is 10 days. The half-life of Ac-225 is 10 days.

## Radioactive Dating

An ingenious application of half-life studies established a new science of determining ages of materials by half-life calculations. For geological dating, the decay of U-238 can be used. The half-life of U-238 is $4.5 \times 10^9$ years. The end product of the decay of U-238 is Pb-206. After one half-life, a 1.00 gram sample of uranium will have decayed to 0.50 grams of U-238 and 0.43 grams of Pb-206. By comparing the amount of U-238 to the amount of Pb-206 in a sample of uranium mineral, the age of the mineral can be estimated. Present day estimates for the age of the Earth's crust from this method is at 4 billion years.

Organic material (material made from things that were once living, such as paper and fabric) is radioactively dated using the long-lived nuclide of carbon, carbon-14. This method of determining the age of organic material (or once living materials) was given the name radiocarbon dating. The carbon dioxide consumed by living systems contains a certain concentration of $^{14}CO_2$. When an organism dies, the acquisition of carbon-14 stops, but the decay of the C-14 in the body continues. As time goes by, the ratio of C-14 to C-12 decreases at a rate determined by the half-life of C-14. Using half-life equations, the time since the organism died can be calculated. These procedures have been used to determine the age of organic artifacts and determine, for instance, whether art works are real or fake.

## Summary and Vocabulary

The half-life of an isotope is used to describe the rate at which the isotope will decay and give off radiation. Using the half-life, it is possible to predict the amount of radioactive material that will remain after a given amount of time. C-14 dating procedures have been used to determine the age of organic artifacts. Its half-life is approximately 5700 years.

- **Background radiation** - Radiation that comes from environmental sources including the earth's crust, the atmosphere, cosmic rays, and radioisotopes. These natural sources of radiation account for the largest amount of radiation received by most people.
- **Half-life** - The time interval required for a quantity of (radioactive) material to decay to half of its original value.

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# 12.3.1: Radiocarbon Dating- Using Radioactivity to Measure the Age of Fossils and Other Artifacts

**Learning Objectives**

- Identify the age of materials that can be approximately determined using Radiocarbon dating.

When we speak of the element Carbon, we most often refer to the most naturally abundant stable isotope $^{12}C$. Although $^{12}C$ is definitely essential to life, its unstable sister isotope $^{14}C$ has become of extreme importance to the science world. Radiocarbon dating is the process of determining the age of a sample by examining the amount of $^{14}C$ remaining against its known half-life, 5,730 years. The reason this process works is because when organisms are alive, they are constantly replenishing their $^{14}C$ supply through respiration, providing them with a constant amount of the isotope. However, when an organism ceases to exist, it no longer takes in carbon from its environment and the unstable $^{14}C$ isotope begins to decay. From this science, we are able to approximate the date at which the organism lived on Earth. Radiocarbon dating is used in many fields to learn information about the past conditions of organisms and the environments present on Earth.

## The Carbon-14 Cycle

Radiocarbon dating (usually referred to simply as carbon-14 dating) is a radiometric dating method. It uses the naturally occurring radioisotope carbon-14 ($^{14}C$) to estimate the age of carbon-bearing materials up to about 58,000 to 62,000 years old. Carbon has two stable, nonradioactive isotopes: carbon-12 ($^{12}C$) and carbon-13 ($^{13}C$). There are also trace amounts of the unstable radioisotope carbon-14 ($^{14}C$) on Earth. Carbon-14 has a relatively short half-life of 5,730 years, meaning that the fraction of carbon-14 in a sample is halved over the course of 5,730 years due to radioactive decay to nitrogen-14. The carbon-14 isotope would vanish from Earth's atmosphere in less than a million years were it not for the constant influx of cosmic rays interacting with molecules of nitrogen ($N_2$) and single nitrogen atoms (N) in the stratosphere. Both processes of formation and decay of carbon-14 are shown in Figure 1.

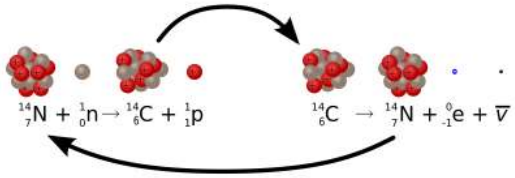



Figure 1: Diagram of the formation of carbon-14 (forward), the decay of carbon-14 (reverse). Carbon-14 is constantly generated in the atmosphere and cycled through the carbon and nitrogen cycles. Once an organism is de-coupled from these cycles (i.e., death), then the carbon-14 decays until there is essentially none left.

When plants fix atmospheric carbon dioxide ($CO_2$) into organic compounds during photosynthesis, the resulting fraction of the isotope $^{14}C$ in the plant tissue will match the fraction of the isotope in the atmosphere (and biosphere since they are coupled). After a plant dies, the incorporation of all carbon isotopes, including $^{14}C$, stops and the concentration of $^{14}C$ declines due to the radioactive decay of $^{14}C$ following.

$$^{14}C \longrightarrow {}^{14}N + e^{-} + \mu_e \tag{12.3.1.1}$$

This follows first-order kinetics:

$$N_t = N_o e^{-kt} \tag{12.3.1.2}$$

where

- $N_0$ is the number of atoms of the isotope in the original sample (at time $t$ = 0, when the organism from which the sample is derived was de-coupled from the biosphere).
- $N_t$ is the number of atoms left after time $t$.
- $k$ is the rate constant for the radioactive decay.

The half-life of a radioactive isotope (usually denoted by $t_{1/2}$) is a more familiar concept than $k$ for radioactivity, so although Equation 12.3.1.2 is expressed in terms of $k$, it is more usual to quote the value of $t_{1/2}$. The currently accepted value for the half-life of $^{14}C$ is 5,730 years. This means that after 5,730 years, only half of the initial $^{14}C$ will remain; a quarter will remain after 11,460 years; an eighth after 17,190 years; and so on.

The equation relating rate constant to half-life for first order kinetics is

$$k = \frac{\ln 2}{t_{1/2}} \tag{12.3.1.3}$$

so the rate constant is then

$$k = \frac{\ln 2}{5.73 \times 10^3} = 1.21 \times 10^{-4} \text{year}^{-1} \tag{12.3.1.4}$$

and Equation 12.3.1.1 can be rewritten as

$$N_t = N_o e^{-\ln 2\, t/t_{1/2}} \tag{12.3.1.5}$$

or

$$t = \left( \frac{\ln \frac{N_o}{N_t}}{\ln 2} \right) t_{1/2} = 8267 \ln \frac{N_o}{N_t} = 19035 \log_{10} \frac{N_o}{N_t} \quad \text{(in years)} \tag{12.3.1.6}$$

The sample is assumed to have originally had the same $^{14}C/^{12}C$ ratio as the ratio in the atmosphere, and since the size of the sample is known, the total number of atoms in the sample can be calculated, yielding $N_0$, the number of $^{14}C$ atoms in the original sample. Measurement of N, the number of $^{14}C$ atoms currently in the sample, allows the calculation of $t$, the age of the sample, using the Equation 12.3.1.6.

**Note**

Deriving Equation 12.3.1.6 assumes that the level of $^{14}C$ in the atmosphere has remained constant over time. However, the level of $^{14}C$ in the atmosphere has varied significantly, so time estimated by Equation 12.3.1.6 must be corrected by using data from other sources.

**Example 1: Dead Sea Scrolls**

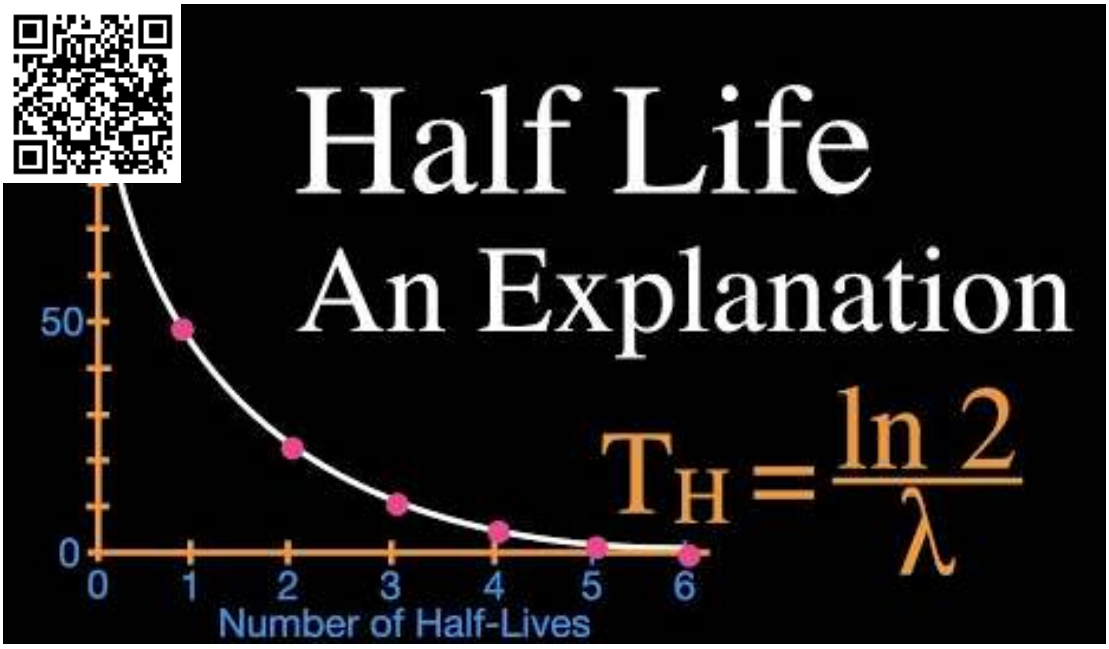
In 1947, samples of the Dead Sea Scrolls were analyzed by carbon dating. It was found that the carbon-14 present had an *activity* (rate of decay) of d/min.g (where d = disintegration). In contrast, living material exhibit an activity of 14 d/min.g. Thus, using Equation 12.3.1.2,

$$\ln \frac{14}{11} = (1.21 \times 10^{-4})t$$

Thus,

$$t = \frac{\ln 1.272}{1.21 \times 10^{-4}} = 2 \times 10^3 \text{years}$$

From the measurement performed in 1947, the Dead Sea Scrolls were determined to be 2000 years old, giving them a date of 53 BC, and confirming their authenticity. This discovery is in contrast to the carbon dating results for the Turin Shroud that was supposed to have wrapped Jesus' body. Carbon dating has shown that the cloth was made between 1260 and 1390 AD. Thus, the Turin Shroud was made over a thousand years after the death of Jesus.




*Describes radioactive half-life and how to do some simple calculations using half-life.*

## History

The technique of radiocarbon dating was developed by Willard Libby and his colleagues at the University of Chicago in 1949. Emilio Segrè asserted in his autobiography that Enrico Fermi suggested the concept to Libby at a seminar in Chicago that year. Libby estimated that the steady-state radioactivity concentration of exchangeable carbon-14 would be about 14 disintegrations per minute (dpm) per gram. In 1960, Libby was awarded the Nobel Prize in chemistry for this work. He demonstrated the accuracy of radiocarbon dating by accurately estimating the age of wood from a series of samples for which the age was known, including an ancient Egyptian royal barge dating from 1850 BCE. Before Radiocarbon dating was discovered, someone had to find the existence of the $^{14}C$ isotope. In 1940, Martin Kamen and Sam Ruben at the University of California, Berkeley Radiation Laboratory did just that. They found a form, an isotope, of Carbon that contained 8 neutrons and 6 protons. Using this finding, Willard Libby and his team at the University of Chicago proposed that Carbon-14 was unstable and underwent a total of 14 disintegrations per minute per gram. Using this hypothesis, the initial half-life he determined was 5568, give or take 30 years. The accuracy of this proposal was proven by dating a piece of wood from an Ancient Egyptian barge, the age of which was already known. From that point on, scientists have used these techniques to examine fossils, rocks, and ocean currents; as well as to determine age and event timing. Throughout the years, measurement tools have become more technologically advanced, allowing researchers to be more precise. We now use what is known as the Cambridge half-life of 5730+/- 40 years for Carbon-14. Although it may be seen as outdated, many labs still use Libby's half-life in order to stay consistent in publications and calculations within the laboratory. From the discovery of Carbon-14 to radiocarbon dating of fossils, we can see what an essential role Carbon has played and continues to play in our lives today.

## Summary

The entire process of Radiocarbon dating depends on the decay of carbon-14. This process begins when an organism is no longer able to exchange Carbon with its environment. Carbon-14 is first formed when cosmic rays in the atmosphere allow for excess neutrons to be produced, which then react with Nitrogen to produce a constantly replenishing supply of carbon-14 to exchange with organisms.

- Carbon-14 dating can be used to estimate the age of carbon-bearing materials up to about 58,000 to 62,000 years old.
- The carbon-14 isotope would vanish from Earth's atmosphere in less than a million years were it not for the constant influx of cosmic rays interacting with atmospheric nitrogen.
- One of the most frequent uses of radiocarbon dating is to estimate the age of organic remains from archeological sites.

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## Problems

1. If, when a hippopotamus lived, there was a total of 25 grams of Carbon-14, how many grams will remain 5730 years after he is laid to rest? 12.5 grams, because one half-life has occurred.
2. How many grams of Carbon-14 will be present in the hippopotamus' remains after three half-lives have passed? 3.125 grams of Carbon-14 will remain after three half-lives.

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# 12.4: The Discovery of Fission and the Atomic Bomb

**Learning Objectives**

- Define and give examples of fission and fusion.
- Classify nuclear reactions as fission or fusion.
- List some medical uses of nuclear energy.

Nuclei that are larger than iron-56 may undergo nuclear reactions in which they break up into two or more smaller nuclei. These reactions are called **fission** reactions. Conversely, nuclei that are smaller than iron-56 become larger nuclei in order to be more stable. These nuclei undergo a nuclear reaction in which smaller nuclei join together to form a larger nucleus. Such nuclear reactions are called **fusion** reactions.

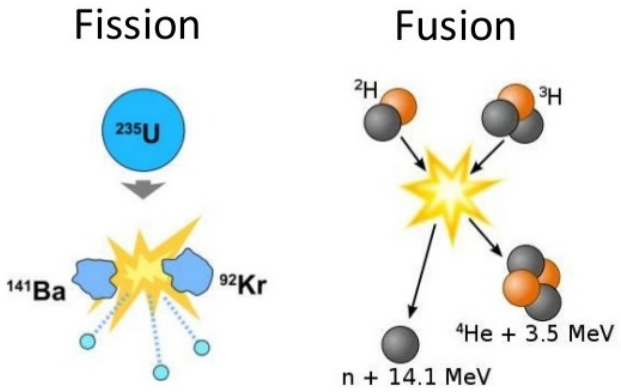



Figure **12.4.1**: (left) Nuclear fission occurs when one large nucleus is split into two or more smaller nuclei. (right) Nuclear fusion happens when two small nuclei combine to make a larger nucleus.

## Fission and Chain Reactions

In both fission and fusion, large amounts of energy are given off in the form of heat, light, and gamma radiation. Nuclear fission was discovered in the late 1930s when U-235 nuclides were bombarded with neutrons and were observed to split into two smaller-mass nuclei.

$$ {}^{1}_{0}\mathrm{n} + {}^{235}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} $$

The products shown are only one of many sets of products from the disintegration of a U-235 nucleus. Over 35 different elements have been observed in the fission products of U-235.

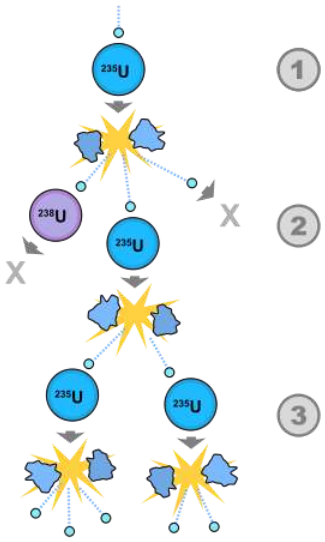



Figure **12.4.2**: A possible nuclear fission chain reaction. 1. A uranium-235 atom absorbs a neutron, and fissions into two new atoms (fission fragments), releasing three new neutrons and a large amount of binding energy. 2. One of those neutrons is absorbed by an atom of uranium-238, and does not continue the reaction. Another neutron leaves the system without being absorbed. However, one neutron does collide with an atom of uranium-235, which then fissions and releases two neutrons and more binding energy. 3. Both of those neutrons collide with uranium-235 atoms, each of which fissions and releases a few neutrons, which can then continue the reaction. (Public Domain.)

When a neutron strikes a **U**-235 nucleus and the nucleus captures a neutron, it undergoes fission, producing two lighter nuclei and three free neutrons. The production of the free neutrons makes it possible to have a self-sustaining fission process—a nuclear **chain reaction**. If at least one of the neutrons goes on to cause another **U**-235 disintegration, the fission will be self-sustaining.

## Nuclear Weapons

It is unfortunate that when the topics of radioactivity and nuclear energy come up, most thoughts probably go to weapons of war. The second thought might be about the possibility of nuclear energy contributing to the solution of the energy crisis. Nuclear energy, however, has many applications beyond bombs and the generation of electricity. Radioactivity has huge applications in scientific research, several fields of medicine both in terms of imaging and in terms of treatment, industrial processes, some very useful appliances, and even in agriculture.

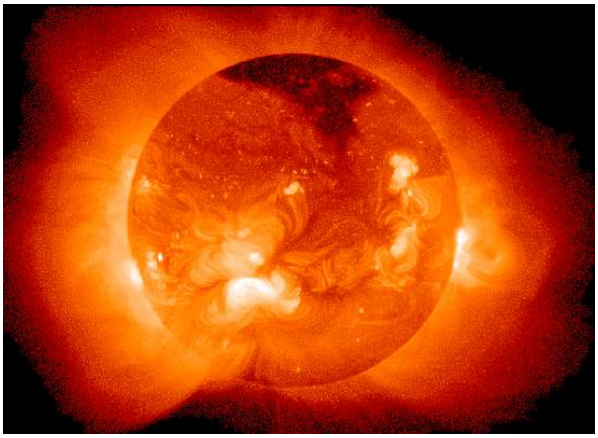


Figure **12.4.3**: The energy that comes from the sun and other stars is produced by fusion. (Public Domain; NASA.)

## Summary and Vocabulary

Naturally radioactive elements exist in the earth and are either alpha or beta emitters. Artificial transmutation of elements can be accomplished by bombarding the nuclei of some elements with alpha or subatomic particles. Nuclear radiation also has many medical uses.

- **Chain reaction** - A multi-stage nuclear reaction that sustains itself in a series of fissions, in which the release of neutrons from the splitting of one atom leads to the splitting of others.
- **Critical mass** - The smallest mass of a fissionable material that will sustain a nuclear chain reaction at a constant level.
- **Fission** - A nuclear reaction in which a heavy nucleus splits into two or more smaller fragments, releasing large amounts of energy.
- **Fusion** - A nuclear reaction in which nuclei combine to form more massive nuclei with the simultaneous release of energy.
- **Control rods** - Rods made of chemical elements capable of absorbing many neutrons, that are used to control the rate of a fission chain reaction in a nuclear reactor.

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# 12.5: Nuclear Power

**Learning Objectives**

- Describe how nuclear fission and fusion generate energy.

## Nuclear Fusion- The Power of the Sun

In addition to fission, a second possible method for obtaining energy from nuclear reactions lies in the fusing together of two light nuclei to form a heavier nucleus. As we see when discussing Figure 1 from Mass-Energy Relationships, such a process results in nucleons which are more firmly bonded to each other, and hence lower in potential energy. This is particularly true if $^{4}_{2}\mathrm{He}$ is formed, because this nucleus is very stable. Such a reaction occurs between the nuclei of the two heavy isotopes of hydrogen, deuterium and tritium:

$$^{2}_{1}\mathrm{D} + {}^{3}_{1}\mathrm{T} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n \tag{12.5.1}$$

For this reaction, $\Delta m = -0.018\ 88\ \mathrm{g\ mol^{-1}}$ so that $\Delta H_m = -1700\ \mathrm{GJ\ mol^{-1}}$. Although very large quantities of energy are released by a reaction like Equation 12.5.1, such a reaction is very difficult to achieve in practice. This is because of the very high activation energy, about 30 GJ $\mathrm{mol^{-1}}$, which must be overcome to bring the nuclei close enough to fuse together. This barrier is created by coulombic repulsion between the positively charged nuclei. The only place where scientists have succeeded in producing fusion reactions on a large scale is in a **hydrogen bomb**. Here, the necessary activation energy is achieved by exploding a fission bomb to heat the reactants to a temperature of about $10^8$ K. Attempts to carry out fusion in a more controlled way have met only limited success. At the very high temperatures required, all molecules dissociate and most atoms ionize. A new state of matter called a **plasma** is formed. It is neither solid, liquid, nor gas. Plasma behaves much like the universal solvent of the alchemists by converting any solid material that it contacts into vapor.

Two techniques for producing a controlled fusion reaction are currently being explored. The first is to restrict the plasma by means of a strong magnetic field, rather than the walls of a container. This has met some success, but has not yet been able to contain a plasma long enough for usable energy to be obtained. The second technique involves the sudden compression and heating of pellets of deuterium and tritium by means of a sharply focused laser beam. Again, only limited success has been obtained.

Though these attempts at a controlled fusion reaction have so far been only partially successful, they are nevertheless worth pursuing. Because of the much readier availability of lighter isotopes necessary for fusion, as opposed to the much rarer heavier isotopes required for fission, controlled nuclear fusion would offer the human race an essentially limitless supply of energy. There would still be some environmental difficulties with the production of isotopes such as tritium, but these would be nowhere near the seriousness of the problem caused by the production of the witches brew of radioactive isotopes in a fission reactor. It must be confessed, though, that at the present rate of progress, the prospect of limitless clean energy from fusion seems unlikely in the next decade or two.

## Nuclear Fission Reactors

Fission reactions can be used in the production of electricity if we control the rate at which the fission occurs. The great majority of all electrical generating systems (whether coal burning power plants, hydroelectric plants, or nuclear power plants) is that they follow a reasonably simple design. The electricity is produced by spinning a coil of wire inside a magnetic field. When a fluid (air, steam, water) is forced through the pipe, it spins the fan blades, which in turn spin the axle. To generate electricity, the axle of a turbine is attached to the loop of wire in a generator. When a fluid is forced through the turbine, the fan blades turn, the turbine axle turns, and the loop of wire inside the generator turns—thus generating electricity.

The essential difference in various kinds of electrical generating systems is the method used to spin the turbine. For a wind generator, the turbine is a windmill. In a geothermal generator, steam from a geyser is forced through the turbine. In hydroelectric generating plants, water falling over a dam passes through the turbine and spins it. In fossil fuel (coal, oil, natural gas) generating plants, the fossil fuel is burned and the heat is used to boil water into steam, and then the steam passes through the turbine to make it spin. In a fission reactor generating plant, a fission reaction is used to boil the water into steam, and the steam passes through the

turbine to make it spin. Once the steam is generated by the fission reaction, a nuclear power plant is essentially the same as a fossil fuel plant.

Naturally occurring uranium is composed almost totally of two uranium isotopes. It contains more than 99% uranium-238 and less than 1% uranium-235. It is the uranium-235, however, that is **fissionable** (will undergo fission). In order for uranium to be used as fuel in a fission reactor, the percentage of uranium-235 must be increased, usually to about 3%. (Uranium in which the U-235 content is more than 1% is called **enriched uranium**.)

Once the supply of U-235 is acquired, it is placed in a series of long cylindrical tubes called fuel rods. These fuel cylinders are bundled together with **control rods** made of neutron-absorbing material. The amount of U-235 in all the fuel rods taken together is adequate to carry on a chain reaction, but is less than the critical mass. (In the United States, all public nuclear power plants contain less than a critical mass of U-235 and therefore, could never produce a nuclear explosion.) The amount of heat generated by the chain reaction is controlled by the rate at which the nuclear reaction occurs. The rate of the nuclear reaction is dependent on how many neutrons are emitted by one U-235 nuclear disintegration *and* strike a new U-235 nucleus to cause another disintegration. The purpose of the control rods is to absorb some of the neutrons and thus stop them from causing further disintegration. The control rods can be raised or lowered into the fuel rod bundle. When the control rods are lowered all the way into the fuel rod bundle, they absorb so many neutrons that the chain reaction essentially stops. When more heat is desired, the control rods are raised so that they catch fewer neutrons, the chain reaction speeds up, and more heat is generated. The control rods are operated in a fail-safe system, so that power is necessary to hold them up; during a power failure, gravity will pull the control rods down into the shut off position.

U-235 nuclei can capture neutrons and disintegrate more efficiently if the neutrons are moving slower than the speed at which they are released. Fission reactors use a moderator surrounding the fuel rods to slow down the neutrons. Water is not only a good coolant, but also a good moderator. A common type of fission reactor has the fuel core submerged in a huge pool of water.

You can follow the operation of an electricity-generating fission reactor in the figure below. The reactor core is submerged in a pool of water. The heat from the fission reaction heats the water and the water is pumped into a heat exchanger container where the heated water boils the water in the heat exchanger. The steam from there is forced through a turbine which spins a generator and produces electricity. After the water passes through the turbine, it is condensed back to liquid water and pumped back to the heat exchanger.

In the United States, heavy opposition to the use of nuclear energy was mounted in the late 1960's and early 1970's. Every environmentalist organization in the US opposed the use of nuclear energy; the constant pressure from environmentalist groups caused an increase of public fear and, therefore, opposition to nuclear energy. This is not true today; at least one environmental leader has published a paper in favor of nuclear-powered electricity generation.

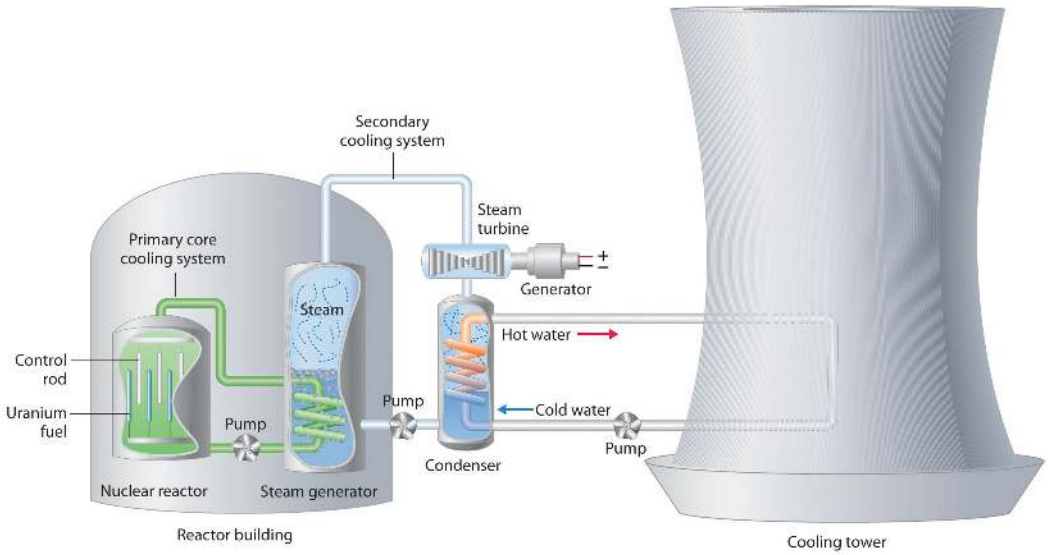



Figure **12.5.1**: A Light-Water Nuclear Fission Reactor for the Production of Electric Power. The fuel rods are made of a corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of $^{235}U$ in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic energy of the neutrons, slowing them to increase the probability that they will induce fission. Control rods that contain elements such as boron, cadmium, or hafnium—which are very effective at absorbing neutrons—are used to control the rate of the fission reaction. A heat exchanger is used to boil water in a secondary cooling system, creating steam to drive the turbine and produce electricity. The large hyperbolic cooling tower, which is the most visible portion of the facility, condenses the steam in the secondary cooling circuit; it is often located at some distance from the actual reactor.

In 1979, a reactor core meltdown at Pennsylvania's Three Mile Island nuclear power plant reminded the entire country of the dangers of nuclear radiation. The concrete containment structure (six feet thick walls of reinforced concrete), however, did what it was designed to do—prevent radiation from escaping into the environment. Although the reactor was shut down for years, there were no injuries or deaths among nuclear workers or nearby residents. Three Mile Island was the only serious accident in the entire history of 103 civilian power plants operating for 40 years in the United States. There has never been a single injury or death due to radiation in any public nuclear power plant in the U.S. The accident at Three Mile Island did, however, frighten the public so that there has not been a nuclear power plant built in the U.S. since the accident.

The 103 nuclear power plants operating in the U.S. deliver approximately **19.4%** of American electricity with zero greenhouse gas emission. There are 600 coal-burning electric plants in the US delivering **48.5%** of American electricity and producing 2 billion tons of $CO_2$ annually, accounting for **40%** of U.S. $CO_2$ emissions and **10%** of global emissions. These coal burning plants also produce **64%** of the sulfur dioxide emissions, **26%** of the nitrous oxide emissions, and **33%** of mercury emissions.

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# 12.6: Biological Effect and Application of Radiation

**Learning Objectives**

- Describe the biological impact of ionizing radiation.
- Define units for measuring radiation exposure.
- Explain the operation of common tools for detecting radioactivity.
- List common sources of radiation exposure in the US.

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure **12.6.1**).

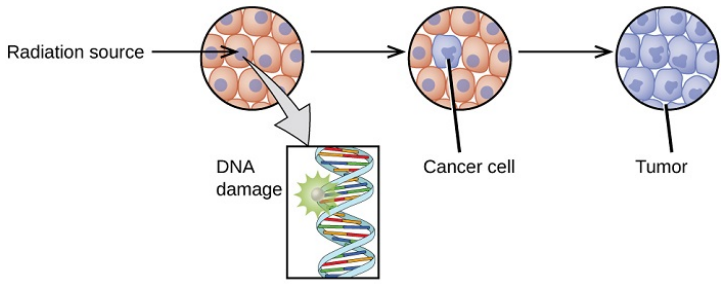



Figure **12.6.1**: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

## Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure **12.6.2**).

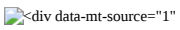



Figure **12.6.2**: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing $H_2O$ (the most abundant molecule in living organisms), which forms a $H_2O^+$ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

$$H_2O + \text{radiation} \xrightarrow{e^-} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\bullet$$

Figure **12.6.3**.

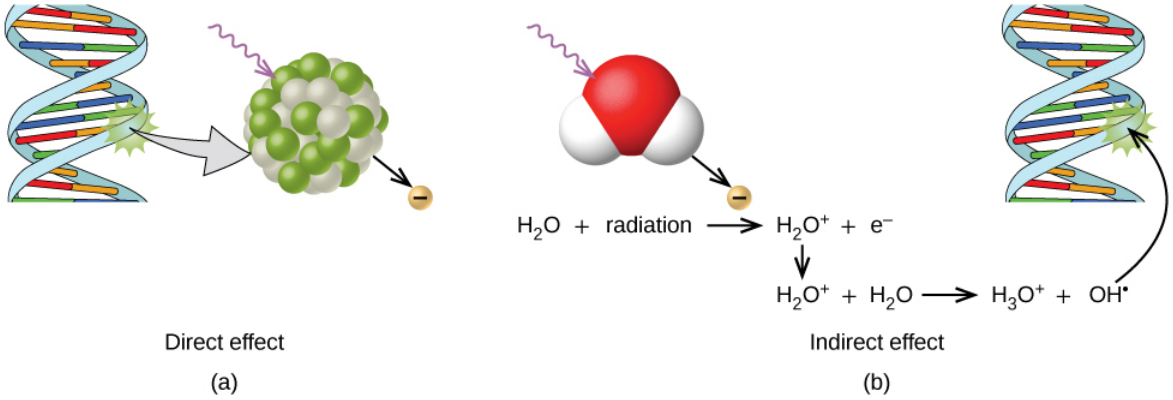



Figure **12.6.3**: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an $H_2O^+$ ion, which reacts with $H_2O$ to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

## Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure **12.6.4**). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

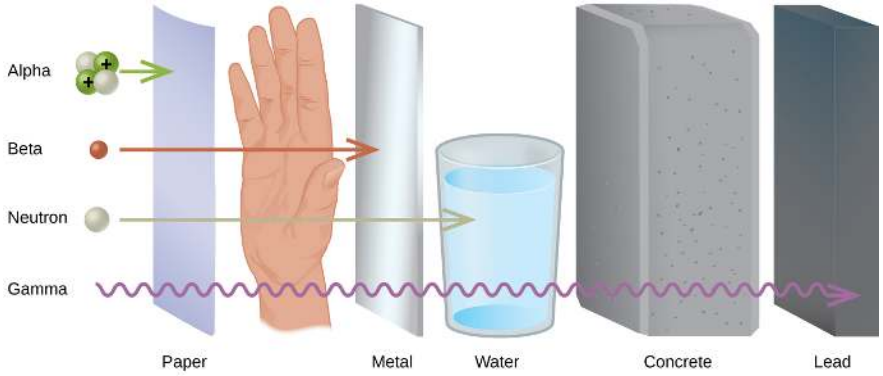



Figure **12.6.4**: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure **12.6.5**).

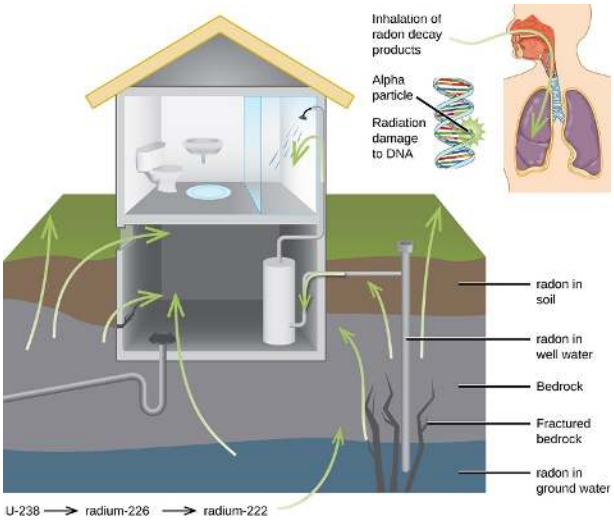



Figure **12.6.5**: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts dependent on location. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the level found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

## Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure **12.6.6**). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

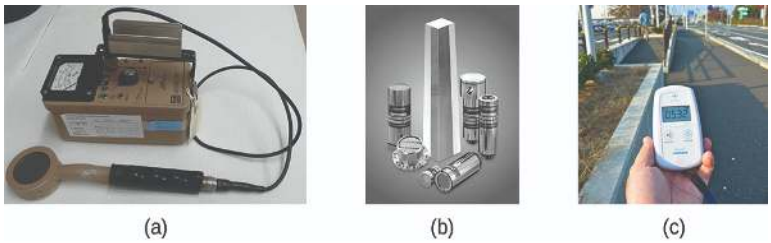



Figure **12.6.6**: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by "osaMu"/Wikimedia commons.)

A variety of units are used to measure various aspects of radiation (Table **12.6.1**). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = $\mathbf{3.7 \times 10^{10}}$ disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table **12.6.1**: Units Used for Measuring Radiation

| Measurement Purpose | Unit | Quantity Measured | Description |
|---|---|---|---|
| *activity of source* | becquerel (Bq) | radioactive decays or emissions | amount of sample that undergoes 1 decay/second |
| | curie (Ci) | | amount of sample that undergoes $3.7 \times 10^{10}$ decays/second |
| *absorbed dose* | gray (Gy) | energy absorbed per kg of tissue | 1 Gy = 1 J/kg tissue |
| | radiation absorbed dose (rad) | | 1 rad = 0.01 J/kg tissue |
| *biologically effective dose* | sievert (Sv) | tissue damage | Sv = RBE × Gy |
| | roentgen equivalent for man (rem) | | Rem = RBE × rad |

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy), along with a biological factor referred to as the RBE (for relative biological effectiveness), that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{12.6.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

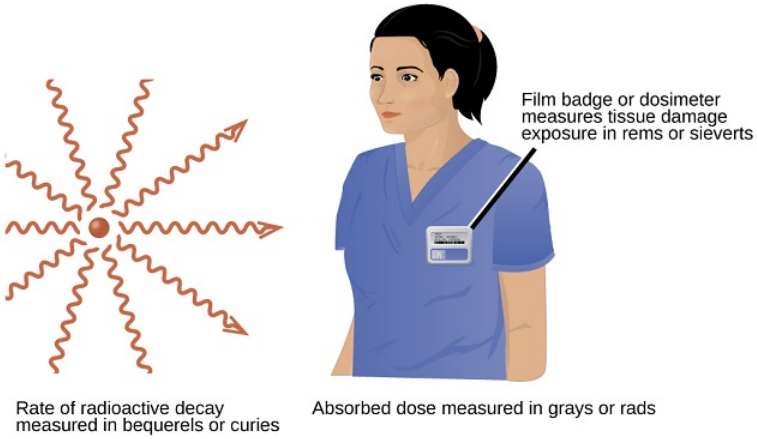



Figure 12.6.7: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC BY 4.0; OpenStax)

### Example 12.6.1: Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

**Solution**

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\ \text{y}}\right) \times 5.00\ \text{g} = 0.659\ \frac{\text{g}}{\text{y}}\ \text{of}\ {}^{60}\text{Co that decay}$$

And to convert this to decays per second:

$$0.659\ \frac{\text{g}}{\text{y}} \times \frac{\text{y}}{365\ \text{day}} \times \frac{1\ \text{day}}{24\ \text{hours}} \times \frac{1\ \text{h}}{3,600\ \text{s}} \times \frac{1\ \text{mol}}{59.9\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{decay}}{1\ \text{atom}}$$

$$= 2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}}$$

(a) Since $1\ \text{Bq} = 1\ \frac{\text{decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left( \frac{1\ \text{Bq}}{1\ \frac{\text{decay}}{\text{s}}} \right) = 2.10 \times 10^{14}\ \text{Bq}$$

(b) Since $1\ \text{Ci} = 3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left( \frac{1\ \text{Ci}}{3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}} \right) = 5.7 \times 10^{2}\ \text{Ci}$$

**? Exercise 12.6.1**

Tritium is a radioactive isotope of hydrogen ($t_{1/2} = 12.32$ years) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

**Answer a**

$3.56 \times 10^{11}\text{Bq}$

**Answer b**

0.962 Ci

## Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure **12.6.8**, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

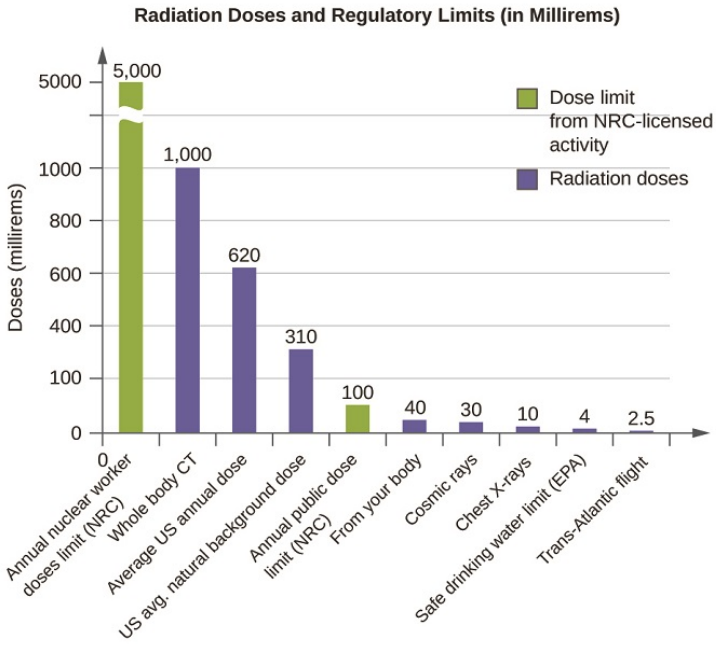



Figure **12.6.8**: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table **12.6.2**.

Table **12.6.2**: Health Effects of Radiation

| Exposure (rem) | Health Effect | Time to Onset (Without Treatment) |
|---|---|---|
| 5–10 | changes in blood chemistry | — |
| 50 | nausea | hours |
| 55 | fatigue | — |
| 70 | vomiting | — |
| 75 | hair loss | 2–3 weeks |
| 90 | diarrhea | — |
| 100 | hemorrhage | — |
| 400 | possible death | within 2 months |
| 1000 | destruction of intestinal lining | — |
| | internal bleeding | — |
| | death | 1–2 weeks |
| 2000 | damage to central nervous system | — |
| | loss of consciousness | minutes |
| | death | hours to days |

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

## Radioisotopes in Medical Diagnosis and Treatment

The molecule picture below is thyroxine, a compound produced by the thyroid gland. This molecule regulates how the body uses energy. In a condition known as hypothyroidism, the thyroid makes less thyroxine than normal. A person with this disease feels tired all the time and often puts on weight. Hypothyroidism is treated with thyroid hormone supplements.

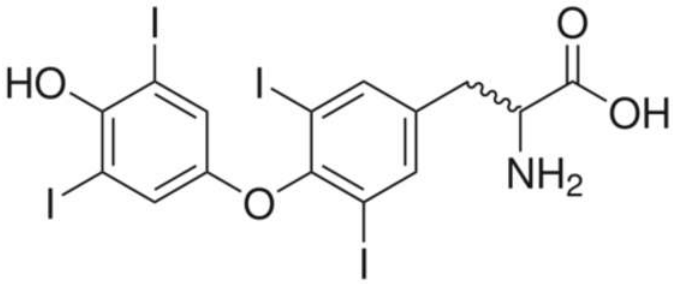



Figure **12.6.7**: Thyroxine molecule.

Radioisotopes are widely used to diagnose disease and as effective treatment tools. For diagnosis, the isotope is administered, and then located in the body using a scanner of some sort. The decay product (often gamma emission) can be located, and the intensity measured. The amount of isotope taken up by the body can then give information as to the extent of the medical problem.

An isotope of iodine (**I**-131) is used in both the diagnosis and treatment of thyroid cancer. The thyroid will normally absorb iodine to produce the iodine-containing thyroid hormones. An overactive thyroid gland will absorb the radioactive material, which can then destroy excess thyroid tissue or any cancer of the thyroid. The material is sometimes used to image cancers in other parts of the body.

Technetium-99m is perhaps the most widely used radioisotope in diagnosis and treatment (the "m" stands for *metastable*). This isotope decays to **Tc**-99 and a gamma emission of low intensity, making the radiation damage fairly negligible. The half-life is about six hours, so it will remain in the body for some time. **Tc**-99m can be used to look at cardiac damage. The isotope flows in the bloodstream; if there is less blood flow in the heart, there will be less isotope concentrated in the heart muscle. Similar information can be obtained for blood flow in the brain.

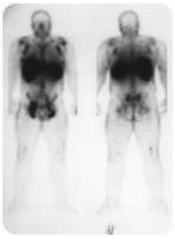


Figure **12.6.8**: Radioisotope scan to detect tumors.

Isotopes can be very useful in scans to locate cancer cells. The patient in the above image has multiple tumors that have spread (metastasized) from the main tumor. A radioisotope has been attached to **antibodies** that bind to specific cancer cells. The very dark spots in the armpits, neck, and groin represent areas where tumor cells exist.

Many other examples could be presented. There are presently over 25 different isotopes in use for diagnosis and treatment. A very partial list can be seen in the table below.

**Table 12.6.3: Radioisotopes Employed in Diagnosis and/or Treatment**

| Isotope | Half-Life | Application |
|---|---|---|
| $^{51}$Cr | 28 days | Label red blood cells. |
| $^{59}$Fe | 446 days | Study iron metabolism in spleen. |
| $^{133}$Xe | 5 days | Study lung function. |
| $^{166}$Ho | 26 hours | Cancer treatment. |

## Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating, but potentially most damaging, and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source of radiation, and limiting time of exposure.

## Footnotes

1. 1 Source: US Environmental Protection Agency

## Glossary

**becquerel (Bq)**
SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s.

**curie (Ci)**
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = $3.7 \times 10^{10}$ disintegrations/s.

**Geiger counter**
Instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube.

**gray (Gy)**
SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue.

**ionizing radiation**
Radiation that can cause a molecule to lose an electron and form an ion.

**millicurie (mCi)**
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = $3.7 \times 10^{10}$ disintegrations/s.

**nonionizing radiation**
Radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules.

**radiation absorbed dose (rad)**

SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy.

**radiation dosimeter**

Device that measures ionizing radiation and is used to determine personal radiation exposure.

**relative biological effectiveness (RBE)**

Measure of the relative damage done by radiation.

**roentgen equivalent man (rem)**

Unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv.

**scintillation counter**

Instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation.

**sievert (Sv)**

SI unit measuring tissue damage caused by radiation; takes energy and biological effects of radiation into account.

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