CHEM 113: HUMAN CHEMISTRY I



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Pedro Muíño

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Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: Matter and Measurements

What is chemistry? Simply put, chemistry is the study of the interactions of matter with other matter and with energy. This seems straightforward enough. However, the definition of chemistry includes a wide range of topics that must be understood to gain a mastery of the topic or even take additional courses in chemistry. In this book, we will lay the foundations of chemistry in a topic-by-topic fashion to provide you with the background you need to successfully understand chemistry.

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1.1: Chemistry - The Central Science

Learning Objectives

- Define chemistry in relation to other sciences.
- Use physical and chemical properties, including phase, to describe matter.

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

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.

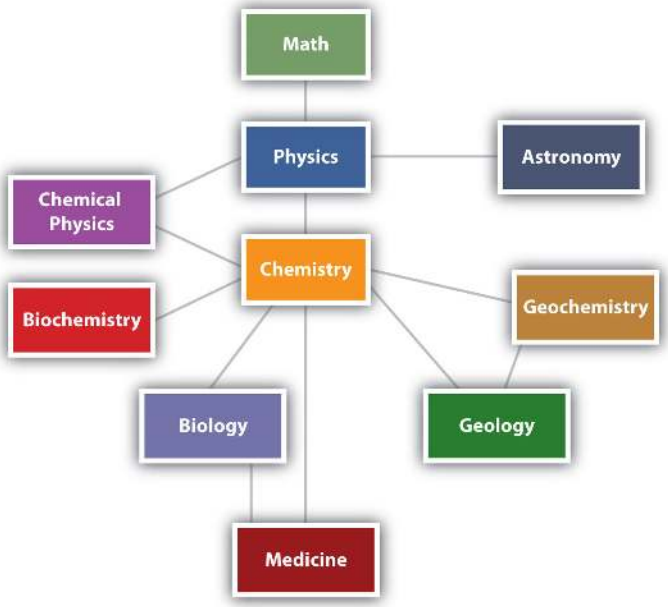


Figure 1.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science. (CC BY-SA-NC; anonymous)

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; there are many other fields of science in addition to the ones listed here.

How do scientists work? Generally, they follow a process called the **scientific method**. The scientific method is an organized procedure for learning answers to questions and making explanations for observations. The steps of the scientific method may not be as clear-cut in real life as described here, but most scientific work follows this general outline.

1. **Propose a hypothesis.** A scientist generates a testable idea, or hypothesis, to try to answer a question or explain an observation about how the natural universe works. Some people use the word *theory* in place of hypothesis, but the word hypothesis is the proper word in science. For scientific applications, the word theory is a general statement that describes a large set of observations and data. A theory represents the highest level of scientific understanding.
2. **Test the hypothesis.** A scientist evaluates the hypothesis by devising and carrying out experiments to test it. If the hypothesis passes the test, it may be a proper answer to the question. If the hypothesis does not pass the test, it may not be a good answer.
3. **Refine the hypothesis if necessary.** Depending on the results of experiments, a scientist may want to modify the hypothesis and then test it again. Sometimes the results show the original hypothesis to be completely wrong, in which case a scientist will

have to devise a new hypothesis.

Not all scientific investigations are simple enough to be separated into these three discrete steps. But these steps represent the general method by which scientists learn about our natural universe.

Physical and Chemical Properties and Changes

The properties that chemists use to describe matter fall into two general categories. **Physical properties** are characteristics that describe matter. They include characteristics such as size, shape, color, and mass. These characteristics can be observed or measured without changing the *identity* of the matter in question. **Chemical properties** are characteristics that describe how matter changes its chemical structure or composition. An example of a chemical property is flammability—a material's ability to burn—because burning (also known as combustion) changes the chemical composition of a material. The observation of chemical properties involves a *chemical change* of the matter in question, resulting in matter with a different *identity* and different physical and chemical properties. Part of understanding matter is being able to describe it. One way chemists describe matter is to assign different kinds of properties to different categories.



Figure 1.1.1: (left) 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 the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (right) Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC SA-BY-3.0; Andrikkos)

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a physical process in which a substance changes from one phase to another. Examples are summarized in Table 1.1.1.

Table 1.1.1: Physical Changes

Change	Name
solid to liquid	melting, fusion
solid to gas	sublimation
liquid to gas	boiling, evaporation
liquid to solid	solidification, freezing
gas to liquid	condensation
gas to solid	deposition

The difference between a physical reaction and a chemical reaction is **composition**. In a chemical reaction, there is a change in the composition of the substances in question; in a **physical change** there is a difference in the appearance, smell, or simple display of a sample of matter without a change in composition. Although we call them physical "reactions," no reaction is actually occurring. In order for a reaction to take place, there must be a change in the elemental composition of the substance in question. Thus, we shall simply refer to "physical reactions" as physical changes from now on.

Example 1.1.1

Classify each of the following changes as physical or chemical:

a. condensation of steam
b. burning of gasoline
c. souring of milk
d. dissolving of sugar in water
e. melting of gold

Solution

The best way to determine whether a change is physical or chemical is to determine if the substance identity has changed or not.

a. Steam is water in the gas phase. When it condenses, changes from gas to liquid, it remains water. Therefore, this is a **physical** change.
b. When gasoline burns, it changes into different substances. This is a **chemical** change.
c. When milk becomes sour, several **chemical** changes have occured; proteins denature, sugars break down, and acid is produced. The milk is now made up of different substances.
d. Sugar dissolves easily into water but it still remains sugar. If the water is evaporated, the sugar will recrystalize as a solid again. Dissolving is a **physical** change, the substance does not change identity.
e. Melting solid gold into liquid gold is a **physical** change much like melting solid water (an ice cube) into liquid water is a physical change.

Exercise 1.1.1

Classify each of the following changes as physical or chemical:

a. coal burning
b. ice melting
c. mixing chocolate syrup with milk
d. explosion of a firecracker
e. magnetizing of a screwdriver

Answer a:
chemical
Answer b:
physical
Answer c:
physical
Answer d:
chemical
Answer e:
physical

Key Takeaways

- Chemistry is the study of matter and how it behaves.
- The scientific method is the general process by which we learn about the natural universe.
- When a substance changes from one state to another, this is a physical change.
- If a substance undergoes a change into one or more different substances, this is a chemical change.

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1.2: States of Matter

Learning Objectives

- Describe the different physical states of matter; solid, liquid, and gas.
- Understand how external conditions can affect the states of matter.

Water can take many forms. At low temperatures (below $0^{o}C$), it is a solid. When at "normal" temperatures (between $0^{o}C$ and $100^{o}C$), it is a liquid. While at temperatures above $100^{o}C$, water is a gas (steam). The state the water is in depends upon the temperature. Each state (solid, liquid, and gas) has its own unique set of physical properties.

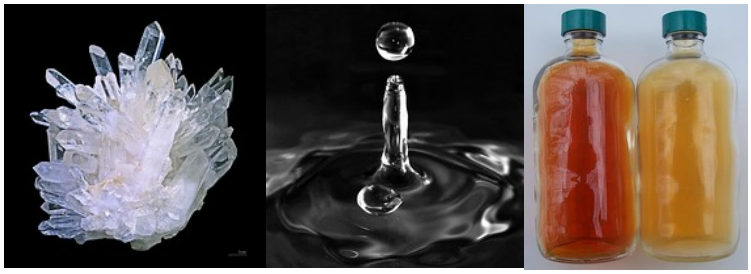


Figure 1.2.1: Matter is usually classified into three classical states. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

Matter typically exists in one of three states: **solid**, **liquid**, or **gas** and these different states of matter have different properties (Table 1.2.1):

- 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. Forces between atoms or molecules are not strong enough to hold them together.
- 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. Forces between atoms or molecules are strong enough to keep the molecules relatively close together but not strong enough to prevent them from moving past 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. Forces between atoms or molecules are strong enough to keep the molecules together and to prevent them from moving past one another.

The state a given substance exhibits is 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 1.2.2 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 (Table 1.2.1).

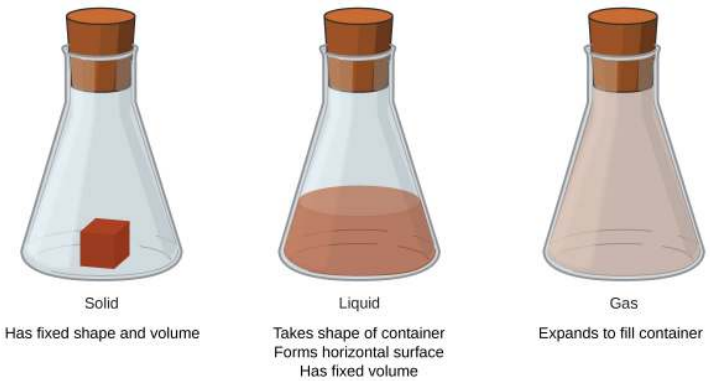


Figure 1.2.2: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

A beaker labeled solid contains a cube of red matter and says has fixed shape and volume. A beaker labeled liquid contains a brownish-red colored liquid. This beaker says takes shape of container, forms horizontal surfaces, has fixed volume. The beaker labeled gas is filled with a light brown gas. This beaker says expands to fill container.

These three descriptions each imply that the matter has certain physical properties when in these states. A solid has a definite shape and a definite volume. Liquids ordinarily have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers. We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas).

Table 1.2.1: Characteristics of each Phase of Matter

	Gas	Liquid	Solid
Shape	no definite shape (takes the shape of its container)	no definite shape (takes the shape of its container)	definite shape (rigid)
Volume	particles move in random motion with little or no attraction to each other	has definite volume	definite volume
Mobility	particles move in random motion with little or no attraction to each other	particles are free to move over each other, but are still attracted to each other	particles vibrate around fixed axes
Compressibility	highly compressible	weakly compressible	weakly compressible

Adding energy to matter gives its atoms or molecules the ability to resist some of the forces holding them together. For example, heating ice to its **melting point** gives its molecules enough energy to move. The ice melts and becomes liquid water. Similarly, heating liquid water to its **boiling point** gives its molecules enough energy to pull apart from one another so they no longer have contact. The liquid water vaporizes and becomes water vapor.

State of Matter Depends on the External Conditions

The temperature of the melting and boiling points depend on the identity of the substance and the atmospheric pressure. Each substance has its own boiling and melting points that depend on the properties of the substance. As an example, the values for water are given in Table 1.2.2. Note how the boiling point of water varies greatly with pressure.

Table 1.2.1: Boiling point of water as a function of pressure

Altitude (ft)	Pressure (atm)	Boiling Point (^{o}C)
-500	1.05	100.5
0	1.00	100
4000	0.892	96
7000	0.797	93

✔ Example 1.2.1

Isopropyl alcohol is a colorless, flammable chemical compound with a strong odor. Its melting point is –89°C and it boiling point is 82.5°C. Is isopropyl alcohol a solid, liquid or gas at room temperature (25°C)?

Solution

Room temperature (25°C) is above the melting point of isopropyl alcohol (–89°C), but lower than its boiling point (82.5°C), therefore, it is a **liquid** at room temperature.

? Exercise 1.2.1

Freon-12 is used as a refrigerant and aerosol spray propellant. Its melting point is –157.7°C and it boiling point is –29.8 °C. Is Freon-12 a solid, liquid or gas at room temperature (25°C).

Answer

> Freon-12 is a **gas** at room temperature

Key Takeaways

- Matter exists in different physical states.
- Changes in conditions such as temperature and pressure can allow matter to change state.

Contributors and Attributions

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1.3: 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 1.3.1). 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.

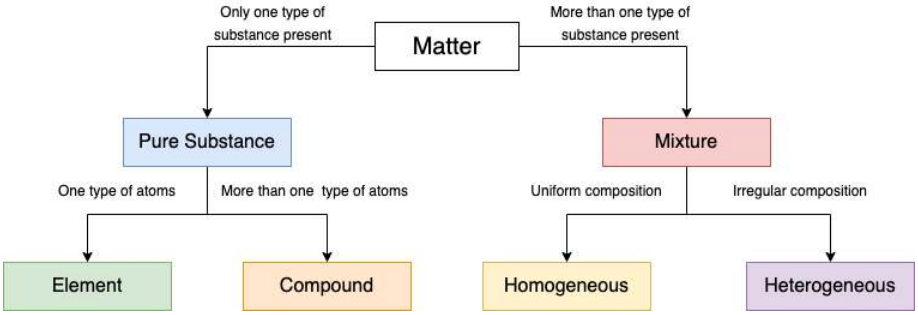


Figure 1.3.1: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.

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 1.3.1). 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 1.3.1).

Example 1.3.1

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

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

Given: a chemical substance

Asked for: its classification

Strategy:

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 1.3.1

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

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

Answer a:

homogeneous mixture (solution)

Answer b:

element

Answer c:

heterogeneous mixture

Answer d:

compound

Example 1.3.2

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 1.3.2

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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1.4: Chemical Elements and Symbols

Learning Objectives

- Identify names and symbols of common chemical elements.
- Represent a chemical compound with a chemical formula.

As described in the previous section, an element is a pure 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 1.4.1 shows some of the chemical elements.



Figure 1.4.1: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

Elemental 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 1.4.1 lists the names and symbols of some of the most familiar elements.

Table 1.4.1: Element Names and Symbols

Element Name	Element Symbol	Element Name	Element Symbol
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*

Element Name	Element Symbol	Element Name	Element Symbol
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.

Elements in Nature and the Human Body

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. On the planet Earth, however, the situation is rather different (Table 1.4.2). 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 1.4.2: Elemental Composition of Earth and the Human Body

Earth's Crust		**Human Body**	
Element	**Percentage**	**Element**	**Percentage**
oxygen	46.1	oxygen	61
silicon	28.2	carbon	23
aluminum	8.23	hydrogen	10
iron	5.53	nitrogen	2.6
calcium	4.15	calcium	1.4
sodium	2.36	phosphorus	1.1
magnesium	2.33	sulfur	0.20
potassium	2.09	potassium	0.20
titanium	0.565	sodium	0.14
hydrogen	0.14	chlorine	0.12
phosphorus	0.105	magnesium	0.027

Earth's Crust		Human Body	
Element	**Percentage**	**Element**	**Percentage**
all others	0.174	silicon	0.026

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

Table 1.4.2 also lists the relative abundances of elements in the human body. If you compare both compositions, 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; carbon is part of the 0.174% representing "other" elements.

How does the human body concentrate so many apparently rare elements? 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: The Phosphorous 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, 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.



Figure 1.4.2: The eutrophication of the Potomac River is evident from the bright green water, caused by a dense bloom of cyanobacteria. (CC BY-SA 3.0; Alexandr Trubetskoy via Wikipedia)

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.

Example 1.4.1

Write the chemical symbol for each element without consulting the above tables.

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

Strategy: The symbol for some of the more common elements is the first one or two letters of the element name. Test yourself to see if you know the symbol, then check your answer in the above tables. You will learn the element symbols as you practice.

Solution

a. Br
b. B
c. C
d. Ca
e. Au

Exercise 1.4.1

Write the chemical symbol for each element without consulting the above tables.

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 1.4.2

What element is represented by each chemical symbol?

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

a. sodium
b.
c. mercury

d.
e. phosphorus
f.
g. potassium
h. iodine
i.

? Exercise 1.4.2

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

Chemical Formulas

A **chemical formula** is an expression that shows each of the elements in a compound and the relative proportions of those elements. Water is composed of hydrogen and oxygen in a 2:1 ratio and its chemical formula is $\mathrm{H_2O}$. Sulfuric acid is one of the most widely produced chemicals in the United States and is composed of the elements hydrogen, sulfur, and oxygen; the chemical formula for sulfuric acid is $\mathrm{H_2SO_4}$. Sucrose (table sugar) consists of carbon, hydrogen, and oxygen in a 12:22:11 ratio. The chemical formula of these are:

$\underbrace{\mathrm{H_2O}}$	$\underbrace{\mathrm{H_2SO_4}}$	$\underbrace{\mathrm{C_{12}H_{22}O_{11}}}$
2 H atoms	2 H atoms	12 H atoms
1 O atom	1 S atom	22 C atoms
	4 O atoms	11 O atoms

Notice that the oxygen and sulfur in water and sulfuric acid, respectively, do not have a "1" subscripts - this is assumed.

Sometimes certain groups of atoms are bonded together within the chemical and act as a single unit. Polyatomic ions will be discussed later and are enclosed in parenthesis followed by a subscript if more than one of the same ion exist in a chemical formula. For example, the formula $\mathrm{Ca_3(PO_4)_2}$ represents a compound with:

- 3 Ca atoms and
- 2 $\mathrm{PO_4^{3-}}$ polyatomic ions

To count the total number of atoms for formulas with polyatomic ions enclosed in parenthesis, use the subscript as a multiplier for each atom or number of atoms.

$$\mathrm{Ca_3(PO_4)_2}$$

and decomposing this to elements gives

- 3 Ca atoms
- 2×1 P atoms
- 2×4 O atoms

That is, 3 Ca atoms, 2 P atoms, and 8 O atoms

Chemical formula can be used in chemical equations. For example, the reaction of hydrogen gas ($\mathrm{H_2}$) burning with oxygen gas ($\mathrm{O_2}$) to form water ($\mathrm{H_2O}$) is written as:

$$2\,\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\,\mathrm{H_2O}$$

? Exercise 1.4.3

Identify the elements in each of the following chemical formulas and what is the ratio of different elements in the chemical formulas:

a. NaOH
b. NaCl
c. $\mathrm{CaCl_2}$
d. $\mathrm{CH_3COOH}$

Answer a

Sodium Na, oxygen O, and hydrogen H are present. This is sodium hydroxide and is also known as lye or caustic soda.

This is a 1:1:1 ratio of sodium, oxygen, and hydrogen, respectively.

Answer b

Sodium Na and chlorine O are present. This is sodium chloride and is also known as table salt.

This is a 1:1 ratio of sodium and chlorine, respectively.

Answer c

Calcium Ca and Chlorine Cl are present. This is calcium chloride and is a different type of salt than sodium chloride.

This is a 1:2 ratio of calcium and chlorine, respectively.

Answer d

Carbon C, Oxygen O, and Hydrogen H are present. This is acetic acid and is also known as vinegar.

This is a 2:2:4 (or 1:1:2) ratio of carbon, oxygen, and hydrogen, respectively.

Key Takeaways

- All matter is composed of elements, which are represented by one- or two-letter symbols.
- Chemical compounds are represented by formulas using element symbols and numerical subscripts to represent the ratio of each element in the compound.

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1.5: Chemical Reactions- Examples of Chemical Change

Chemical reactions are the processes by which chemicals interact to form new chemicals with different compositions. Simply stated, a chemical reaction is the process where reactants are transformed into products. How chemicals react is dictated by the chemical properties of the element or compound- the ways in which a compound or element undergoes changes in composition.

Chemical reactions are constantly occurring in the world around us; everything from the rusting of an iron fence to the metabolic pathways of a human cell are all examples of chemical reactions. Chemistry is an attempt to classify and better understand these reactions. One key reaction in modern civilization is combustion



Figure 1.5.1: An ignited lighter showing the combustion of butane. (Public Domain; Kimmo Palosaari via Wikipedia)

A chemical reaction is typically represented by a **chemical equation**, which represents the change from reactants to products. The left hand side of the equation represents the **reactants**, while the right hand side represents the **products**. A typical chemical reaction is written with stoichiometric coefficients, which show the relative amounts of products and reactants involved in the reaction. Each compound is followed by a parenthetical note of the compound's physical state: (l) for liquid, (s) for solid, (g) for gas. The symbol (aq) is also commonly used in order to represent an aqueous solution, in which compounds are dissolved in water.

Butane is a gas at room temperature and atmospheric pressure and is highly flammable, colorless, easily liquefied gas (under light pressure). Butane can be used for gasoline blending, as a fuel gas, fragrance extraction solvent, either alone or in a mixture with propane, and as a feedstock for the manufacture of ethylene and butadiene, a key ingredient of synthetic rubber. The chemical formula of butane if $\mathrm{C_4H_{10}}$. When oxygen is plentiful, butane burns to form carbon dioxide and water vapor as observed in modern lighters (Figure 1.5.1).

This reaction in words is:

$$\text{butane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water} \tag{1.5.1}$$

and the corresponding chemical equation for this reaction is:

$$2\,\mathrm{C_4H_{10}(g)} + 13\,\mathrm{O_2(g)} \rightarrow 8\,\mathrm{CO_2(g)} + 10\,\mathrm{H_2O(g)} \tag{1.5.2}$$

In the above chemical equation, $\mathrm{C_4H_{10}}$ and $\mathrm{O_2}$ are the **reactants** that reacted to form the **products**: $\mathrm{CO_2}$ and $\mathrm{H_2O}$,

Writing Chemical Equations

To write an accurate chemical equation, two things must occur:

1. Each product and reactant must be written using its chemical formula
2. Coefficients are used in front of the chemical formulas to reflect the ratio species (discussed further in a later chapter)
3. Adding the phase of each chemical in parentheses (although this is often dropped for convenience)

Key Takeaways

- Chemical reactions are written to represent chemical changes.
- Chemical formulas are used to represent the reactants (starting substance) and the products (the new substances).

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1.6: 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 1.6.1); the nurse is also measuring.



Figure 1.6.1: 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 1.6.1

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 1.6.2

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).

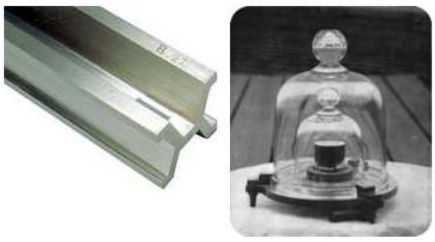


Figure 1.6.2: Meter standard (left) and Kilogram standard (right).

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 1.6.1.

Table 1.6.1: 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.

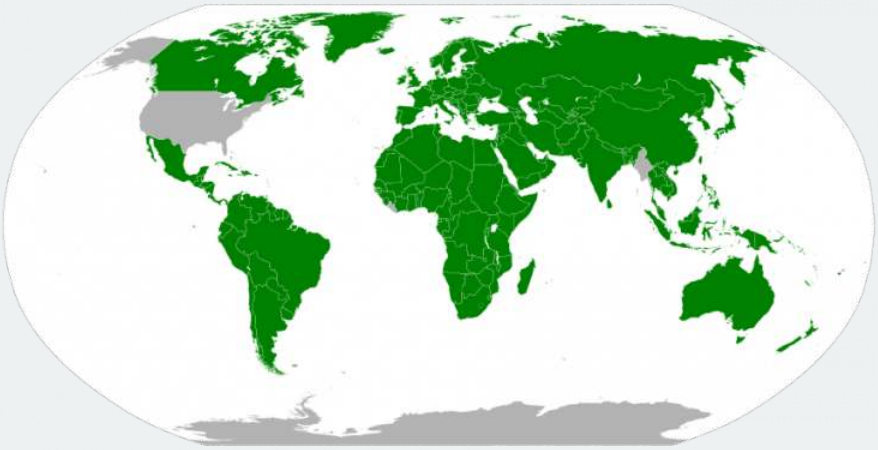


Figure 1.6.2: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

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 $\mu\varepsilon\gamma\alpha\varsigma$, meaning "great". Table 1.6.2 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 1.6.2: SI Prefixes. Commonly used prefixes are bolded.

Prefix	Unit Abbreviation	Meaning	Example
giga	G	1,000,000,000	1 gigameter $(\mathrm{Gm}) = 10^9$ m
mega	M	1,000,000	1 megameter $(\mathrm{Mm}) = 10^6$ m
kilo	k	**1,000**	**1 kilo**meter $(\mathrm{km}) = \mathbf{1,000}$ m
hecto	h	100	1 hectometer $(\mathrm{hm}) = 100$ m
deka	da	10	1 dekameter $(\mathrm{dam}) = 10$ m
		1	1 meter (m)
deci	d	**1/10**	**1 deci**meter $(\mathrm{dm}) = \mathbf{0.1}$ m
centi	c	**1/100**	**1 centi**meter $(\mathrm{cm}) = \mathbf{0.01}$ m
milli	m	**1/1,000**	**1 milli**meter $(\mathrm{mm}) = \mathbf{0.001}$ m
micro	$\boldsymbol{\mu}$	**1/1,000,000**	**1 micro**meter $(\boldsymbol{\mu}\mathrm{m}) = \mathbf{10^{-6}}$ m
nano	n	1/1,000,000,000	1 nanometer $(\mathrm{nm}) = 10^{-9}$ m
pico	p	1/1,000,000,000,000	1 picometer $(\mathrm{pm}) = 10^{-12}$ 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 $3.5\ \mathrm{mL}$.

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 6.5 kg, this is easier than saying it weighs 6500 g or 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 1.6.2: 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

	Explanation	Answer
d	The prefix nano means 1/1000000000, so a nanogram is equal to 0.000000001 g	ng

? Exercise 1.6.2

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

$$N \times 10^n \tag{1.6.1}$$

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 1.6.1.

✓ Example 1.6.1: 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 Because the decimal point was moved two places to the left, n = 2.	6.378×10^{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 Because the decimal point was moved two places to the right, n = −2.	4.79×10^{-2}
c	This is usually expressed simply as 7.86. (Recall that $10^{0} = 1$.)	7.86×10^{0}
d	Because the decimal point was moved four places to the left, n = 4.	1.2378×10^{4}
e	Because the decimal point was moved four places to the right, n = −4.	3.2×10^{-4}
f	Because the decimal point was moved one place to the left, n = 1.	6.106700×10^{1}
g	Because the decimal point was moved three places to the left, n = 3.	2.002080×10^{3}
h	Because the decimal point was moved two places to the right, n = -2.	1.020×10^{-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 $1.6.2$ illustrates how to do this.

Example 1.6.2: 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

	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.	4.87×10^3
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.	6.047×10^{-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 1.6.3.

Example 1.6.3: 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 38.7×10^{21} to scientific notation, n has become more positive by 1 because the value of N has decreased.	3.87×10^{22}

	Explanation	Answer
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 0.183×10^{4} to scientific notation, n has become more negative by 1 because the value of N has increased.	1.83×10^{3}
c	This problem has both multiplication and division: $\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \frac{39.78}{8.52} \times 10^{[-34+1-(-2)]}$	4.7×10^{-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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1.7: Measuring Mass, Length, and Volume

Learning Objective

- Describe the units (and abbreviations) that go with various quantities.
- Derive new units by combining numerical prefixes with units.

Mass vs. Weight

One of the many interesting things about travel in outer space is the idea of weightlessness. If something is not fastened down, it will float in mid-air. Early astronauts learned that weightlessness had bad effects on bone structure. If there was no pressure on the legs, those bones would begin to lose mass. Weight provided by gravity is needed to maintain healthy bones. Specially designed equipment is now a part of every space mission so the astronauts can maintain good body fitness.

Mass is a measure of the amount of matter that an object contains. The mass of an object is made in comparison to the standard mass of 1 kilogram. The kilogram was originally defined as the mass of $1\ \mathrm{L}$ of liquid water at $4^{\circ}\mathrm{C}$ (volume of a liquid changes slightly with temperature). In the laboratory, mass is measured with a balance (see below), which must be calibrated with a standard mass so that its measurements are accurate.



Figure 1.7.1: An analytical balance makes very sensitive mass measurements in a laboratory, usually in grams.

Other common units of mass are the gram and the milligram. A gram is 1/1000th of a kilogram, meaning that there are $1000\ \mathrm{g}$ in $1\ \mathrm{kg}$. A milligram is 1/1000th of a gram, so there are $1000\ \mathrm{mg}$ in $1\ \mathrm{g}$.

The Difference Between Mass and Weight

The mass of a body is a measure of its inertial property or how much matter it contains. The weight of a body is a measure of the force exerted on it by gravity or the force needed to support it. Gravity on earth gives a body a downward acceleration of about 9.8 $\mathrm{m/s^2}$. In common parlance, weight is often used as a synonym for mass in weights and measures. For instance, the verb “to weigh” means “to determine the mass of” or “to have a mass of.” The incorrect use of weight in place of mass should be phased out, and the term mass used when mass is meant. The SI unit of mass is the kilogram (kg). In science and technology, the weight of a body in a particular reference frame is defined as the force that gives the body an acceleration equal to the local acceleration of free fall in that reference frame. Thus, the SI unit of the quantity weight defined in this way (force) is the newton (N).

Length

Length is the measurement of the extent of something along its greatest dimension. The SI basic unit of length, or linear measure, is the **meter** (m). All measurements of length may be made in meters, though the prefixes listed in various tables will often be more convenient. The width of a room may be expressed as about 5 meters (m), whereas a large distance, such as the distance between New York City and Chicago, is better expressed as 1150 kilometers (km). Very small distances can be expressed in units such as the millimeter or the micrometer. The width of a typical human hair is about 10 micrometers $(\mu\mathrm{m})$.

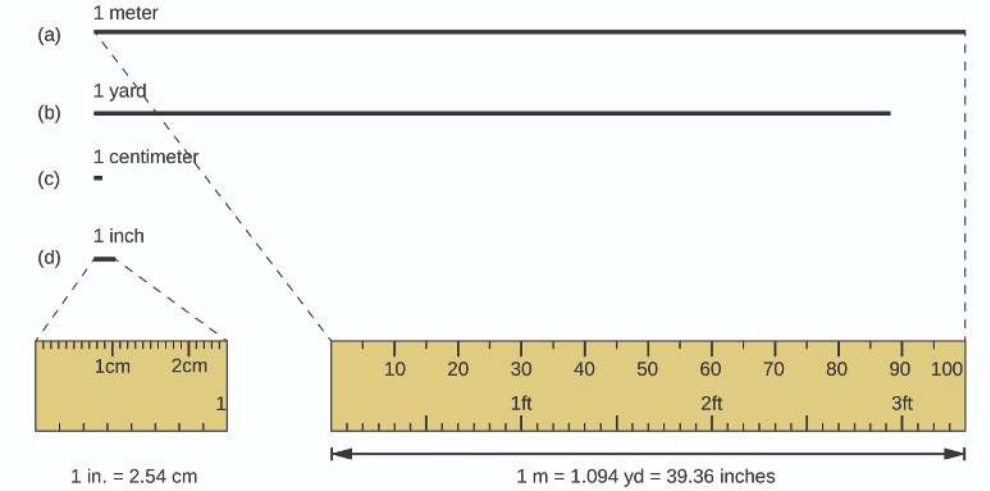


Figure 1.7.2: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

Volume

In addition to the fundamental units, SI also allows for **derived** units based on a fundamental unit or units. There are many derived units used in science. For example, the derived unit for *area* comes from the idea that area is defined as width times height. Because both width and height are lengths, they both have the fundamental unit of meter, so the unit of area is meter × meter, or meter^2 (m^2). This is sometimes spoken as "square meters." A unit with a prefix can also be used to derive a unit for area, so we can also have cm^2, mm^2, or km^2 as acceptable units for area.

Volume is the amount of space occupied by a sample of matter. The volume of a regular object can be calculated by multiplying its length by its width and its height. Since each of those is a linear measurement, we say that units of volume are derived from units of length. One unit of volume is the cubic meter $\left(\mathrm{m}^3\right)$, which is the volume occupied by a cube that measures 1 m on each side. This very large volume is not very convenient for typical use in a chemistry laboratory. A liter (L) is the volume of a cube that measures 10 cm $(1\ \mathrm{dm})$ on each side. A liter is thus equal to both 1000 cm^3 $(10\ \mathrm{cm} \times 10\ \mathrm{cm} \times 10\ \mathrm{cm})$ and to 1 dm^3. A smaller unit of volume that is commonly used is the milliliter (mL - note the capital L which is a standard practice). A milliliter is the volume of a cube that measures 1 cm on each side. Therefore, a milliliter is equal to a cubic centimeter $\left(\mathrm{cm}^3\right)$. There are 1000 mL in 1 L, which is the same as saying that there are 1000 cm^3 in 1 dm^3.

Another definition of a liter is one-tenth of a meter cubed. Because one-tenth of a meter is 10 cm, then a liter is equal to 1,000 cm^3 (Figure 1.7.3). Because 1 L equals 1,000 mL, we conclude that 1 mL equals 1 cm^3; thus, these units are interchangeable.

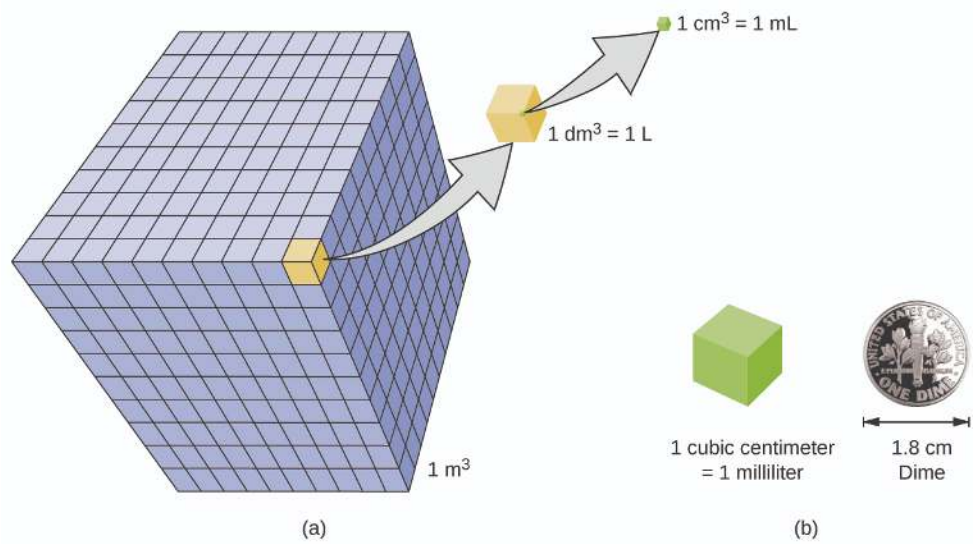


Figure 1.7.3: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube. (CC BY 4.0; OpenStax)

Units not only are multiplied together but also can be divided. For example, if you are traveling at one meter for every second of time elapsed, your velocity is 1 meter per second, or 1 m/s. The word *per* implies division, so velocity is determined by dividing a distance quantity by a time quantity. Other units for velocity include kilometers per hour (km/h) or even micrometers per nanosecond (μm/ns). Later, we will see other derived units that can be expressed as fractions.

Key Takeaways

- Mass is a measure of the amount of matter that an object contains. Mass is independent of location.
- Weight is a measure of force that is equal to the gravitational pull on an object. Weight depends on location.
- Units can be multiplied and divided to generate new units for quantities like the liter for volume.

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1.8: Measurement and Significant Figures

Learning Objectives

- Identify the number of significant figures in a reported value.
- Apply the concept of significant figures to report a measurement with the proper number of digits.

Scientists have established certain conventions for communicating the degree of **precision** of a measurement, which is dependent on the measuring device used (See Figure 1.8.1). Imagine, for example, that you are using a meterstick to measure the width of a table. The centimeters (cm) marked on the meterstick, tell you how many *centimeters* wide the table is. Many metersticks also have markings for millimeters (mm), so we can measure the table to the nearest *millimeter*. The measurement made using millimeters is more precise, it is closer to the actual length of the table. Most metersticks do not have any smaller (or more precise) markings indicated, so you cannot report the measured width of the table any more precise than to the nearest millimeter.

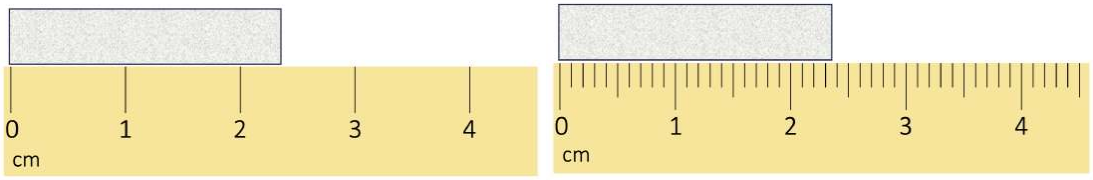


Figure 1.8.1: Different measuring devices have different degrees of **precision**. The ruler on the left has centimeter markings and the measurement of the box is 2.3 cm. Here, the first digit is *certain*, and the second digit is *estimated*, there are two digits reported for this measurement. The ruler on the right has millimeter markings (1/10 of a centimeter) and the measurement of the box is 2.36 cm. Here, the first two digits are *certain*, and the third digit is *estimated*, there are three digits reported for this measurement. The ruler on the right is more precise than the ruler on the left because more digits are reported. (Figure: Lisa Sharpe Elles)

The concept of **significant figures** takes the limitation of measuring devices into account. The significant figures of a measured quantity are defined as **all** the digits known with *certainty* (those indicated by the markings on the measuring device) *and* the *first* uncertain, or estimated, digit (one digit past the smallest marking on the measuring device). It makes no sense to estimate and report any digits after the first uncertain one, so it is the last significant digit reported in a measurement. Zeros are used when needed to place the significant figures in their correct positions. Thus, zeros are sometimes counted as significant figures but are sometimes only used as placeholders (see the rules for significant figures below for more details).

> *"Sig figs" is a common abbreviation for significant figures.*

Rules for Determination of Significant Figures

Consider the earlier example of measuring the width of a table with a meterstick. If the table is measured and reported as being 1,357 mm wide, the number 1,357 has four significant figures. The 1 (thousands place), the 3 (hundreds place), and the 5 (tens place) are certain; the 7 (ones place) is assumed to have been estimated. It would make no sense to report such a measurement as 1,357.0 (five Sig Figs) or 1,357.00 (six Sig Figs) because that would suggest the measuring device was able to determine the width to the nearest tenth or hundredth of a millimeter, when in fact it shows only tens of millimeters and therefore the ones place was estimated.

On the other hand, if a measurement is reported as 150 mm, the 1 (hundreds) and the 5 (tens) are known to be significant, but how do we know whether the zero is or is not significant? The measuring device could have had marks indicating every 100 mm or marks indicating every 10 mm. How can you determine if the zero is significant (the estimated digit), or if the 5 is significant and the zero a value placeholder?

The **rules** for deciding which digits in a measurement are significant are as follows:

Rule 1: All nonzero digits in a measurement are significant.

- 237 has three significant figures.
- 1.897 has four significant figures.

Rule 2: Zeros that appear between other nonzero digits (i.e., "**middle zeros**") are always significant.

- 39,004 has five significant figures.
- 5.02 has three significant figures.

Rule 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.
- 0.000416 has three significant figures.

Rule 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.

- 1400 is ambiguous.
  - 1.4×10^3 has two significant figures.
  - 1.40×10^3 three significant figures.
  - 1.400×10^3 has four significant figures.

Rule 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.
- 19.000 has five significant figures.

It needs to be emphasized that just because a certain digit is not significant does not mean that it is not important or that it can be left out. Though the zero in a measurement of 140 may not be significant, the value cannot simply be reported as 14. An insignificant zero functions as a placeholder for the decimal point. When numbers are written in scientific notation, this becomes more apparent. The measurement 140 can be written as 1.4×10^2, with two significant figures in the coefficient or as 1.40×10^3, with three significant figures. A number less than one, such as 0.000416, can be written in scientific notation as 4.16×10^{-4}, which has 3 significant figures. In some cases, scientific notation is the only way to correctly indicate the correct number of significant figures. In order to report a value of 15,000,00 with four significant figures, it would need to be written as 1.500×10^7.

Exact Quantities

When numbers are known exactly, the significant figure rules do not apply. This occurs when objects are counted rather than measured. For example, a carton of eggs has 12 eggs. The actual value cannot be 11.8 eggs, since we count eggs in whole number quantities. So the 12 is an exact quantity. Exact quantities are considered to have an *infinite number* of significant figures; the importance of this concept will be seen later when we begin looking at how significant figures are dealt with during calculations. Numbers in many conversion factors, especially for simple unit conversions, are also exact quantities and have infinite significant figures. There are exactly 100 centimeters in 1 meter and exactly 60 seconds in 1 minute. Those values are definitions and are not the result of a measurement.

Example 1.8.2

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 explaining how many significant figures are in each number.

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

Explanation	Answer
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 1.8.2

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 figure.

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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1.9: Rounding Off Numbers

Learning Objectives

- 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 $1.9.1$.

Table 1.9.1: 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.*

Rules for Calculations With Measured Numbers

How are significant figures handled in calculations? It depends on what type of calculation is being performed.

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:

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

38.65 times 105.93 equals 4094.1954, which should be rounded to 4 sig figs since the lowest count in the numbers being multiplied is 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 4.5×10^2, whereas 450.0 has four significant figures and would be written as 4.500×10^2. In scientific notation, all significant figures are listed explicitly.

Example 1.9.1

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

a. 23.096×90.300
b. 125×9.000

Solution

a

Solution to (a) in example question.

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.	2.0856×10^3

b

Solution to (b) in example question.

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

Addition and Subtraction

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.

$$\begin{array}{r} 77.2 \\ \underline{10.46} \\ 87.66 \end{array}$$

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

Example 1.9.2

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

Solution

a

Solution to (a) in example question.

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

Solution to (b) in example question.

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 1.9.2

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

Example 1.9.3

a. 2(1.008g) + 15.99 g
b. 137.3 s + 2(35.45 s)
c. $\frac{118.7g}{2} - 35.5g$

Solution

a

Solution to (a) in example question.

Explanation	Answer
2(1.008g) + 15.99 g = **Perform multiplication first.** 2 (1.008g *4 sig figs*) = **2.016 g** *4 sig figs* The number with the least number of significant figures is 1.008g; *the number 2 is an exact number and therefore has infinite number of significant figures*. **Then, perform the addition.** **2.016 g** *thousandths place* + 15.99 g *hundredths place (least precise)* = 18.006 g **Round the final answer.** 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

Solution to (b) in example question.

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

c

Solution to (c) in example question.

Explanation	Answer

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

Exercise 1.9.3

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 sig. figs. 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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1.10: 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:

$$\frac{3.55}{1} \times \frac{100 \text{ cm}}{1} = 355 \text{ cm} \tag{1.10.1}$$

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 1.10.1), 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 1.10.1shows a **concept map** for constructing a proper conversion.

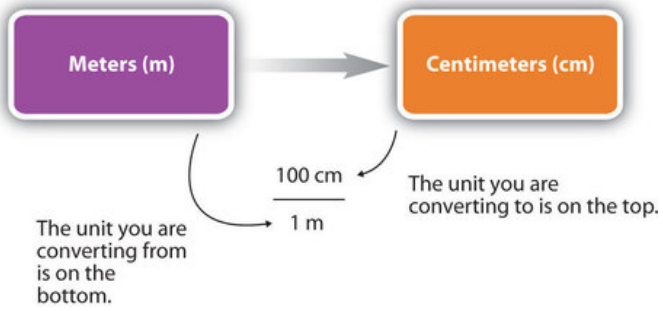


Figure 1.10.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Meters converted to centimeters. A fraction showing 100 cm over 1 m. The unit you convert to is on top, and the unit you convert from is on bottom.

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 1.10.1

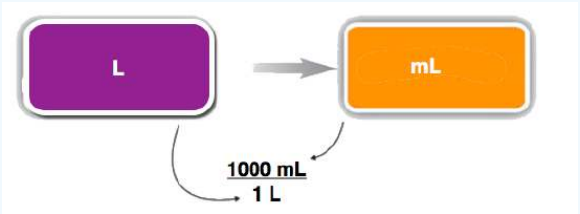
a. The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?
b. A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?

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:

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

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.



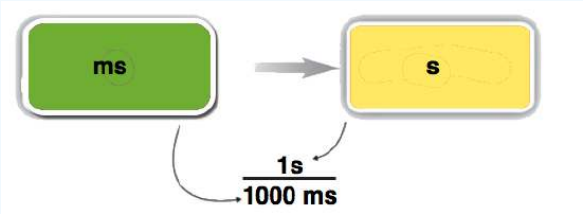
$$4.7 \text{ L} \times \frac{1,000 \text{ mL}}{1 \text{ L}} = 4,700 \text{ mL}$$

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:



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

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

? Exercise 1.10.1

Perform each conversion.

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

Answer a

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

Answer b

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

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 1.10.2: 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 1.10.2

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 $1,000$ mm for every 1 m:

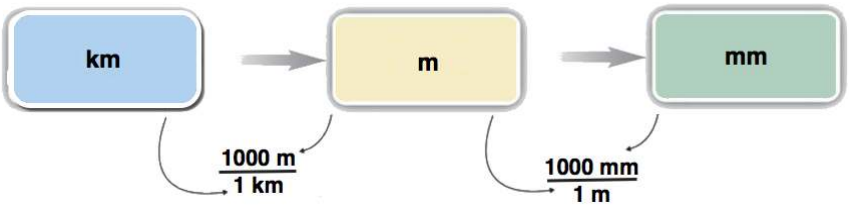
$$54,700 \ \cancel{\text{m}} \times \frac{1,000 \text{ mm}}{1 \ \cancel{\text{m}}} = 54,700,000 \text{ mm}$$

$$= 5.47 \times 10^7 \text{ mm}$$

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.

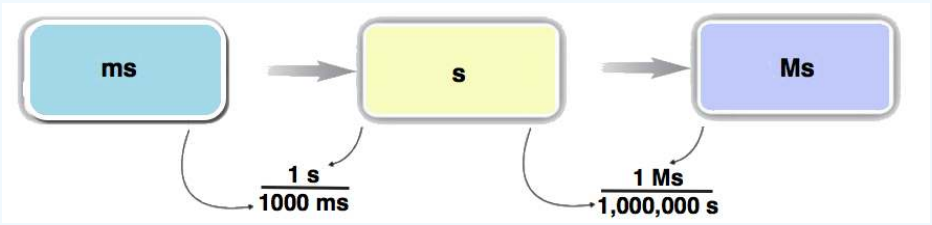
Example 1.10.3

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 1.10.3

Convert 43.007 mg to kilograms in one multistep calculation.

Answer

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

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

https://chem.libretexts.org/@go/page/402611

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 1.0×10^{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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1.11: Temperature, Heat, and Energy

Learning Objectives

- To identify the different between temperature and heat
- To recognize the different scales used to measuring temperature

Temperature

Temperature is a measure of the average kinetic energy of the particles in matter. In everyday usage, temperature indicates a measure of how hot or cold an object is. Temperature is an important parameter in chemistry. When a substance changes from solid to liquid, it is because there was in increase in the temperature of the material. Chemical reactions usually proceed faster if the temperature is increased. Many unstable materials (such as enzymes) will be viable longer at lower temperatures.



Figure 1.11.1: The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

Three different scales are commonly used to measure temperature: 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 1.11.2: Daniel Gabriel Fahrenheit (left), Anders Celsius (center), and Lord Kelvin (right)

The Fahrenheit Temperature Scale

The first thermometers were glass and contained alcohol, which expanded and contracted as the temperature changed. The German scientist, Daniel Gabriel Fahrenheit used mercury in the tube, an idea put forth by Ismael Boulliau. The Fahrenheit scale was first developed in 1724 and tinkered with for some time after that. The main problem with this scale is the arbitrary definitions of temperature. The freezing point of water was defined as 32°F and the boiling point as 212°F. The Fahrenheit scale is typically not used for scientific purposes.

The Celsius Temperature Scale

The Celsius scale of the metric system is named after Swedish astronomer Anders Celsius (1701 - 1744). The Celsius scale sets the freezing point and boiling point of water at 0°C and 100°C respectively. The distance between those two points is divided into 100 equal intervals, each of which is one degree. Another term sometimes used for the Celsius scale is "centigrade" because there are 100 degrees between the freezing and boiling points of water on this scale. However, the preferred term is "Celsius".

The Kelvin Temperature Scale

The Kelvin temperature scale is named after Scottish physicist and mathematician Lord Kelvin (1824 - 1907). It is based on molecular motion, with the temperature of $0\ \text{K}$, also known as **absolute zero**, being the point where all molecular motion ceases. The freezing point of water on the Kelvin scale is $273.15\ \text{K}$, while the boiling point is $373.15\ \text{K}$. Notice that there is no "degree"

used in the temperature designation. Unlike the Fahrenheit and Celsius scales where temperatures are referred to as "degrees F" or "degrees C", we simply designated temperatures in the Kelvin scale as kelvin.

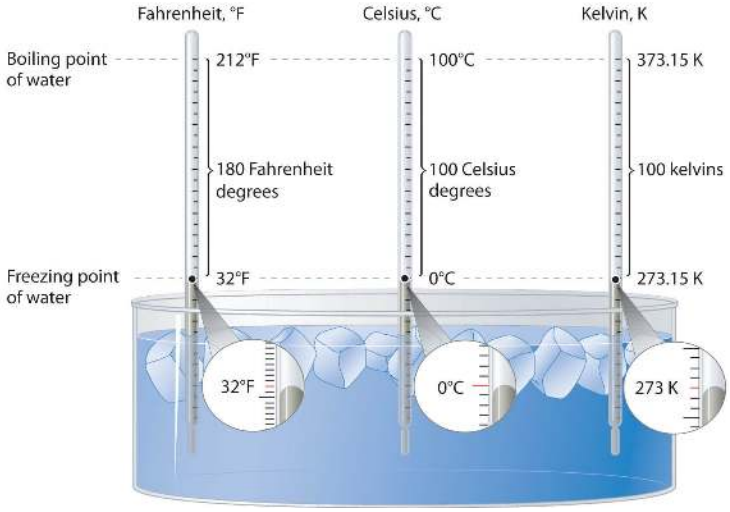


Figure 1.11.3: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (CC BY-SA-NC 3.0; anonymous)

The Kelvin is the same size as the Celsius degree, so measurements are easily converted from one to the other. The freezing point of water is 0°C = 273.15 K; the boiling point of water is 100°C = 373.15 K. The Kelvin and Celsius scales are related as follows:

$$T\,(\text{in }^\circ\text{C}) + 273.15 = T\,(\text{in K}) \tag{3.10.1}$$

$$T\ \ (\text{in K}) - 273.15 = T\ (\text{in }^\circ\text{C}) \tag{3.10.2}$$

Degrees on the Fahrenheit scale, however, are based on an English tradition of using 12 divisions, just as 1 ft = 12 in. The relationship between degrees Fahrenheit and degrees Celsius is as follows: where the coefficient for degrees Fahrenheit is exact. (Some calculators have a function that allows you to convert directly between °F and °C.) There is only one temperature for which the numerical value is the same on both the Fahrenheit and Celsius scales: −40°C = −40°F. The relationship between the scales are as follows:

$$^\circ C = \frac{5}{9} \times (^\circ F - 32) \tag{3.10.3}$$

$$^\circ F = \frac{9}{5} \times (^\circ C) + 32 \tag{3.10.4}$$

Example 1.11.1: Temperature Conversions

A student is ill with a temperature of 103.5°F. What is her temperature in °C and K?

Solution

Converting from Fahrenheit to Celsius requires the use of Equation 3.10.3:

$$\begin{aligned} ^\circ C &= \frac{5}{9} \times (103.5\,^\circ F - 32) \\ &= 39.7\,^\circ C \end{aligned}$$

Converting from Celsius to Kelvin requires the use of Equation 3.10.1:

$$\begin{aligned} K &= 39.7\,^\circ C + 273.15 \\ &= 312.9\,K \end{aligned}$$

? Exercise 1.11.1

Convert each temperature to °C and °F.

a. the temperature of the surface of the sun (5800 K)
b. the boiling point of gold (3080 K)
c. the boiling point of liquid nitrogen (77.36 K)

Answer (a)

5527 K, 9980 °F

Answer (b)

2807 K, 5084 °F

Answer (c)

-195.79 K, -320.42 °F

Heat

While the concept of temperature may seem familiar to you, many people confuse temperature with heat. as discussed above, **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 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.

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're awake or asleep.

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 $1^{\circ}\mathrm{C}$. For example, raising the temperature of $100\ \mathrm{g}$ of water from $20^{\circ}\mathrm{C}$ to $22^{\circ}\mathrm{C}$ 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 $85\ \mathrm{kcal}$ or $85,000\ \mathrm{cal}$ In order to make the distinction, the dietary calorie is written with a capital C.

$$1\ \text{kilocalorie} = 1\ \text{Calorie} = 1000\ \text{calories} \tag{1.11.1}$$

To say that the snack "contains" 85 Calories means that $85\ \mathrm{kcal}$ 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.

$$1\ \mathrm{J} = 0.2390\ \mathrm{cal}\ \text{or}\ 1\ \mathrm{cal} = 4.184\ \mathrm{J} \tag{1.11.2}$$

We can calculate the amount of heat released in kilojoules when a 400. Calorie hamburger is digested.

$$400\ \mathrm{Cal} = 400\ \mathrm{kcal} \times \frac{4.184\ \mathrm{kJ}}{1\ \mathrm{kcal}} = 1.67 \times 10^{3}\ \mathrm{kJ} \tag{1.11.3}$$

Heat Capacity and Specific Heat

If a swimming pool and wading pool, both full of water at the same temperature, were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. Because of its much larger mass, the swimming pool of water has a larger "heat capacity" than the wading pool. Similarly, different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot.

We would say that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$). Water is very resistant to changes in temperature, while metals in general are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$. The symbol for specific heat is c_p, with the p subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree $\left(\mathrm{J/g^{\circ}C}\right)$ or calories per gram per degree $\left(\mathrm{cal/g^{\circ}C}\right)$ (Table 1.11.1). This text will use $\mathrm{J/g^{\circ}C}$ for specific heat.

$$\text{specific heat} = \frac{\text{heat}}{\text{mass} \times \mathrm{cal/g^{\circ}C}} \tag{1.11.4}$$

Notice that water has a very high specific heat compared to most other substances.

Table 1.11.1: Specific Heat Capacities

Substance	Specific Heat Capacity at 25ºC in J/g ºC	Substance	Specific Heat Capacity at 25ºC in J/g ºC
$\mathrm{H_2}$ gas	14.267	steam @ 100ºC	2.010
He gas	5.300	vegetable oil	2.000
$\mathrm{H_2O(l)}$	4.184	sodium	1.23
lithium	3.56	air	1.020
ethyl alcohol	2.460	magnesium	1.020
ethylene glycol	2.200	aluminum	0.900
ice @ 0oC	2.010	Concrete	0.880
steam @ 100oC	2.010	glass	0.840

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 1.11.4: 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.

Example 1.11.1: Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$\begin{aligned} q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184 \text{ J/ } \cancel{\text{g}}^\circ\text{C}) \times (800 \ \cancel{\text{g}}) \times (85 - 21)^\circ\text{C} \\ &= (4.184 \text{ J/ } \cancel{\text{g}}^\circ \ \cancel{\text{C}}) \times (800 \ \cancel{\text{g}}) \times (64)^\circ \ \cancel{\text{C}} \\ &= 210,000 \text{ J} (= 210 \text{ kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive

Exercise 1.11.1

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

5.05×10^4 J

Summary

- Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K).
- Heat capacity is the amount of heat required to raise the temperature of an object by 1°C).
- 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.

Contributions & Attributions

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1.12: Density and Specific Gravity

Learning Objectives

- Define density and specific gravity.
- Perform calculations involving both density and specific gravity.

After trees are cut, logging companies often move these materials down a river to a sawmill where they can be shaped into building materials or other products. The logs float on the water because they are less dense than the water they are in. Knowledge of density is important in the characterization and separation of materials. Information about density allows us to make predictions about the behavior of matter.

Density

A golf ball and a table tennis ball are about the same size. However, the golf ball is much heavier than the table tennis ball. Now imagine a similar size ball made out of lead. That would be very heavy indeed! What are we comparing? By comparing the mass of an object relative to its size, we are studying a property called **density**. Density is the ratio of the mass of an object to its volume.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.12.1}$$

$$D = \frac{m}{V} \tag{1.12.2}$$

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 $1.12.1$.

Table 1.12.1: Densities of Some Common Substances

Liquids and Solids	Density at 20°C (g/mL)	Gases	Density at 20°C (g/L)
Ethanol	0.79	Hydrogen	0.084
Ice (0°C)	0.917	Helium	0.166
Corn oil	0.922	Air	1.20
Water	0.998	Oxygen	1.33
Water (4°C)	1.000	Carbon dioxide	1.83
Corn syrup	1.36	Radon	9.23
Aluminum	2.70		
Copper	8.92		
Lead	11.35		
Mercury	13.6		
Gold	19.3		

The SI units of density are kilograms per cubic meter $\left(\text{kg}/\text{m}^3\right)$, since the kg and the m are the SI units for mass and length respectively. In everyday usage in a laboratory, this unit is awkwardly large. Most solids and liquids have densities that are conveniently expressed in grams per cubic centimeter $\left(\text{g}/\text{cm}^3\right)$. Since a cubic centimeter is equal to a milliliter, density units can also be expressed as g/mL. Gases are much less dense than solids and liquids, so their densities are often reported in g/L. Water has a density of $1.0\ \text{g}/\text{mL}$

File:Separatory_funnel_with_oil_and_colored_water.jpgfile
File:Separatory_funnel_with_oil_and_colored_water.jpg



Figure 1.12.1: Separatory Funnel containing oil and colored water to display density differences. (CC BY-SA 3.0; PRHaney vai Wikipedia).

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 1.12.1), the volume units will cancel and leave you with mass units, telling you the mass of the sample:

Start with Equation 1.12.1

$$\text{density} = \frac{m}{V}$$

and insert the relavant numbers

$$\frac{2.7g}{cm^3} = \frac{m}{7.88\,cm^3}$$

Cross multiplying both sides (right numerator x left denominator = left numerator x right denominator), we get the following expression with answer and appropriate unit.

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

Since most materials expand as temperature increases, the density of a substance is temperature dependent and usually decreases as temperature increases. You known that ice floats in water and it can be seen from the table that ice is less dense. Alternatively, corn syrup, being denser, would sink if placed in water.

Example 1.12.1

An 18.2 g sample of zinc metal has a volume of 2.55 cm^3. Calculate the density of zinc.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Mass = 18.2 g
- Volume = 2.55 cm^3

Unknown

- Density = ? g/cm^3

Use Equation 1.12.1 to solve the problem.

Step 2: Calculate

$$D = \frac{m}{V} = \frac{18.2\ \text{g}}{2.55\ \text{cm}^3} = 7.14\ \text{g/cm}^3 \tag{1.12.3}$$

Step 3: Think about your result.

If 1 cm^3 of zinc has a mass of about 7 grams, then 2 and a half cm^3 will have a mass about 2 and a half times as great. Metals are expected to have a density greater than that of water and zinc's density falls within the range of the other metals listed above.

Since density values are known for many substances, density can be used to determine an unknown mass or an unknown volume. Dimensional analysis will be used to ensure that units cancel appropriately.

Example 1.12.2

1. What is he mass of $2.49\ \text{cm}^3$ of aluminum?
2. What is the volume of $50.0\ \text{g}$of aluminum?

Solution

Step 1: List the known quantities and plan the problem.

Known

- Density $= 2.70\ \text{g/cm}^3$
- 1. Volume $= 2.49\ \text{cm}^3$
- 2. Mass $= 50.0\ \text{g}$

Unknown

- 1. Mass $=?\ \text{g}$
- 2. Volume $=?\ \text{cm}^3$

Use the equation for density, $D = \frac{m}{V}$, and dimensional analysis to solve each problem.

Step 2: Calculate

$$1.\ \ 2.49\ \text{cm}^3 \times \frac{2.70\ \text{g}}{1\ \text{cm}^3} = 6.72\ \text{g} \tag{1.12.4}$$

$$2.\ \ 50.0\ \text{g} \times \frac{1\ \text{cm}^3}{2.70\ \text{g}} = 18.5\ \text{cm}^3 \tag{1.12.5}$$

In problem 1, the mass is equal to the density multiplied by the volume. In problem 2, the volume is equal to the mass divided by the density.

Step 3: Think about your results.

Because a mass of 1 cm^3 of aluminum is $2.70\ \text{g}$, the mass of about $2.5\ \text{cm}^3$ should be about 2.5 times larger. The $50\ \text{g}$ of aluminum is substantially more than its density, so that amount should occupy a relatively large volume.

Specific Gravity

Specific gravity is the ratio of the density (mass of a unit volume) of a substance to the density of a given reference material, often a liquid.

$$\text{specific gravity} = \frac{\text{Density of a substance}(\ g/\cancel{mL})}{\text{Density of the water at the same temperature}(\ g/\cancel{mL})} \tag{1.12.6}$$

If a substance's relative density is less than one then it is less dense than water and similarly, if greater than 1 then it is denser than water. If the relative density is exactly 1 then the densities are equal. For example, an ice cube, with a relative density of about 0.91, will float on water and a substance with a relative density greater than 1 will sink.

A *hydrometer* is an instrument used for measuring the specific density of liquids based on the concept of buoyancy (Figure 1.12.2). A hydrometer usually consists of a sealed hollow glass tube with a wider bottom portion for buoyancy, a ballast such as lead or mercury for stability, and a narrow stem with graduations for measuring. The liquid to test is poured into a tall container, often a graduated cylinder, and the hydrometer is gently lowered into the liquid until it floats freely. The point at which the surface of the liquid touches the stem of the hydrometer correlates to relative density. Hydrometers can contain any number of scales along the stem corresponding to properties correlating to the density.



Figure 1.12.2: A US Navy Aviation Boatswain's Mate tests the specific gravity of JP-5 fuel. (Public Domain; U.S. Navy via Wikipedia)

Summary

- Density is the ratio of the mass of an object to its volume.
- Gases are less dense than either solids or liquids.
- Both liquid and solid materials can have a variety of densities.
- For liquids and gases, the temperature will affect the density to some extent.

Contributors and Attributions

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CHAPTER OVERVIEW

2: Atoms and the Periodic Table

2.1: Atomic Theory and the Structure of Atoms
2.2: Elements and Atomic Number
2.3: Isotopes and Atomic Weight
2.4: The Periodic Table
2.5: Some Characteristics of Different Groups
2.6: Electronic Structure of Atoms
2.7: Electron Configurations
2.8: Electron Configurations and the Periodic Table
2.9: Electron-Dot Symbols

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2.1: Atomic Theory and the Structure of Atoms

Learning Objectives

- State the modern atomic theory.
- Describe how atoms are constructed.

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, 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 5.4×10^{-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 2.1.1 summarizes the properties of these three subatomic particles.

Table 2.1.1: Properties of the Three Subatomic Particles

Name	Symbol	Mass (approx.; g)	Mass (approx.; amu)	Charge
Proton	p^+	1.673×10^{-24}	1.0073	+1
Neutron	n, n^0	1.675×10^{-24}	1.0087	none
Electron	e^-	9.109×10^{-28}	5.486×10^{-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 = 1.660539×10^{-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 2.1.1: Electrons are *much smaller* than protons or neutrons. If an electron was the mass of a penny (right), a proton or a neutron would have the mass of a large bowling ball (left)!

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 2.1.2). Because protons and neutrons are so massive compared to electrons, Table 2.1.1, nearly all of the mass of an atom is contained in the nucleus.

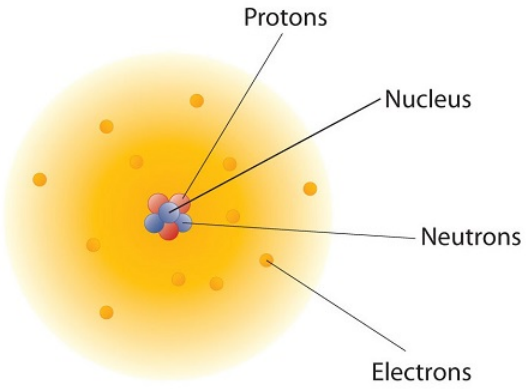


Figure 2.1.2: The Structure of the Atom. Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.

Note 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 2.1.1, control of individual atoms can be use used create animations.



Video 2.1.1: 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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2.2: Elements and Atomic Number

Learning Objectives

- Use the atomic number and mass number to describe an atom.

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 later chapters.

$$atomic\,number - Z - p^{+} - e^{-1} \tag{2.2.1}$$

As we learned previously, 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:

$$mass\,number - A - p^{+} + n \tag{2.2.2}$$

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 will be discussed in more detail in the next chapter.

Example 2.2.1

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.

Exercise 2.2.1

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

Example 2.2.2 :

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 $^{235}_{92}\text{U}$

b. This iron atom has 26 protons and 56 − 26 = 30 neutrons.

Exercise 2.2.2

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

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.

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2.3: 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 2.3.1 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.

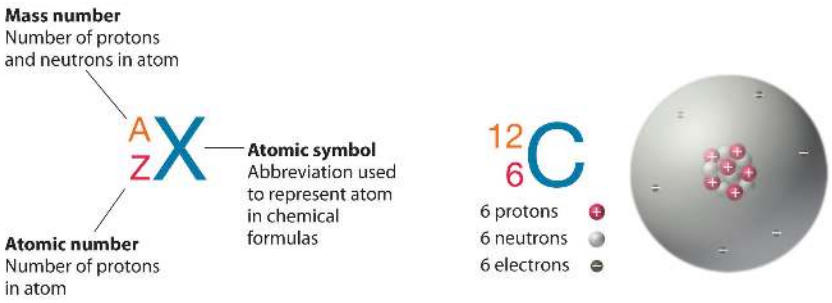


Figure 2.3.1: Nuclear Symbol. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons 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 2.3.2 compares the three isotopes of hydrogen.

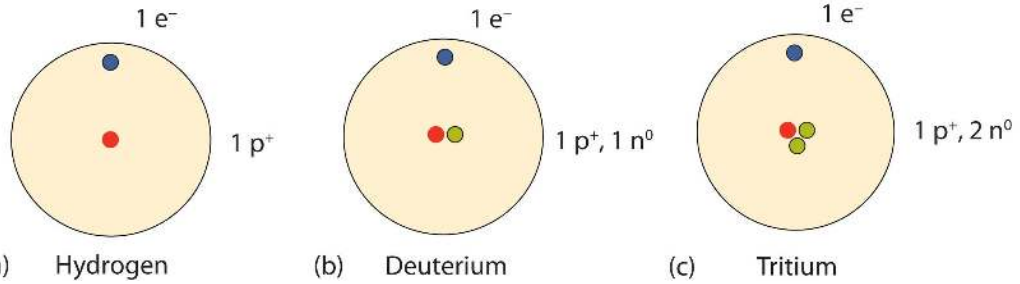


Figure 2.3.2: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, 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 2.3.1. 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 2.3.1

Common Name	A/Z formats	symbol-mass format	Expanded Name
Hydrogen	${}^{1}_{1}\mathrm{H}$	H-1	hydrogen-1
Deuterium	${}^{2}_{1}\mathrm{H}$	H-2	hydrogen-2
Tritium	${}^{3}_{1}\mathrm{H}$	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 2.3.2 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:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots \tag{2.3.1}$$

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 $10\ \text{amu}$. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of $11\ \text{amu}$. How do we calculate the atomic mass of boron?

Boron has two isotopes so we will use the Equation 2.3.1 and substitute the relative abundances and atomic masses of Boron into Equation 2.3.1:

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

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

Example 2.3.1: 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 2.3.1

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 2.3.3: 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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2.4: 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 2.4.1. 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.

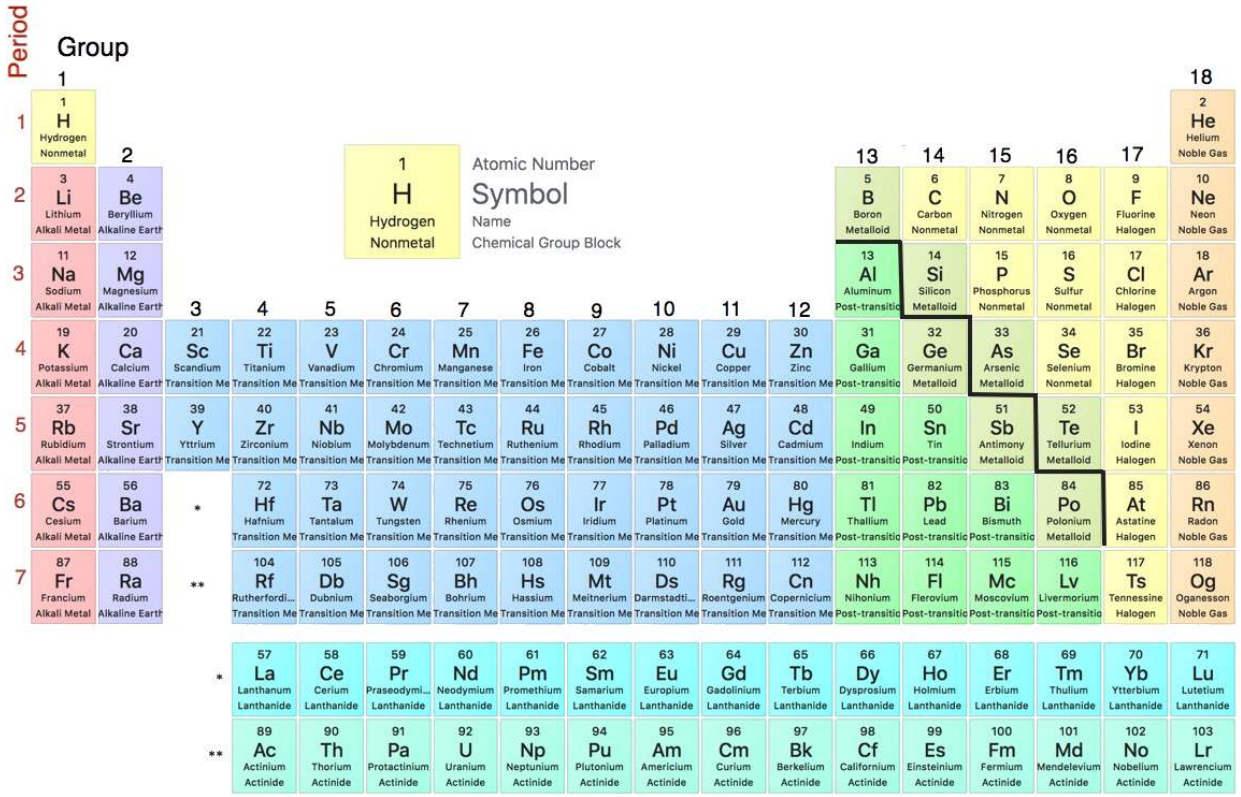


Figure 2.4.1: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares). An interactive Periodic table can be found here.

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 2.4.2. 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 2.4.2, **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.

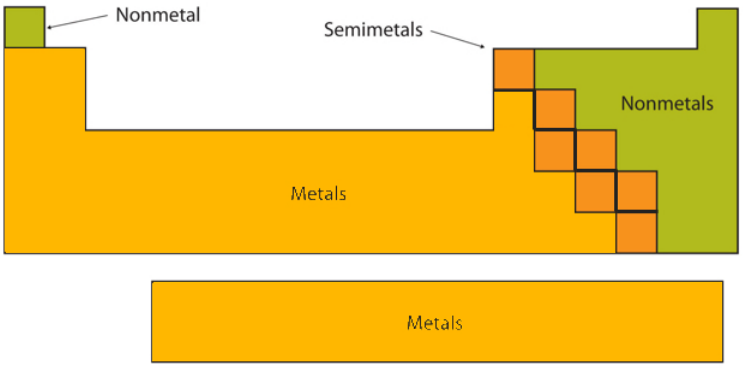


Figure 2.4.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 2.4.1

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 2.4.2, 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 2.4.1

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 2.4.3. 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.

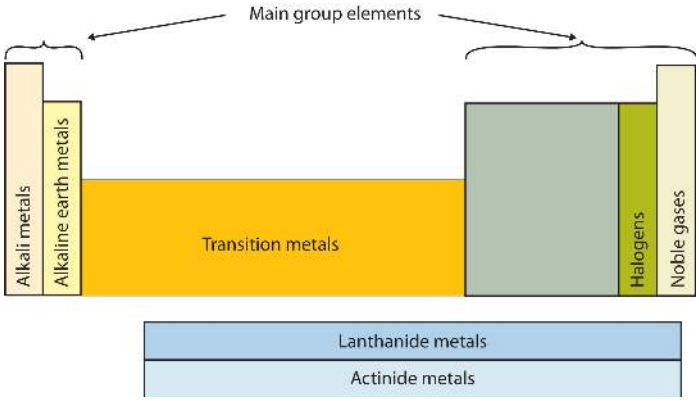


Figure 2.4.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

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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2.5: Some Characteristics of Different Groups

Learning Objectives

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

The periodic table is useful for understanding atomic properties that show **periodic trends**. Periodic trends are specific patterns that are present in the periodic table that illustrate different aspects of a certain element, including its size and its electronic properties. Major periodic trends include atomic radius, melting point, among many other properties as we will discuss. Periodic trends, arising from the arrangement of the periodic table, provide chemists with an invaluable tool to quickly predict an element's properties. These trends exist because of the similar atomic structure of the elements within their respective group families or periods, and because of the periodic nature of the elements.

One important atomic property is the **atomic radius**, which is a measure of the atomic size, usually the distance from the nucleus to the out electron shell. However, since this boundary is not well-defined, there are multiple definitions of atomic radius. Irrespective of the definition used, a clear periodic trend can be observed when atomic radius is plotted vs. atomic number (Figure 2.5.1). The radii generally decrease along each row of the table and increase down each group. The radius increases sharply between the noble gas at the end of each period and the alkali metal at the beginning of the next period. The largest atoms are found in the lower left corner of the periodic table and the smallest are found in the upper right corner

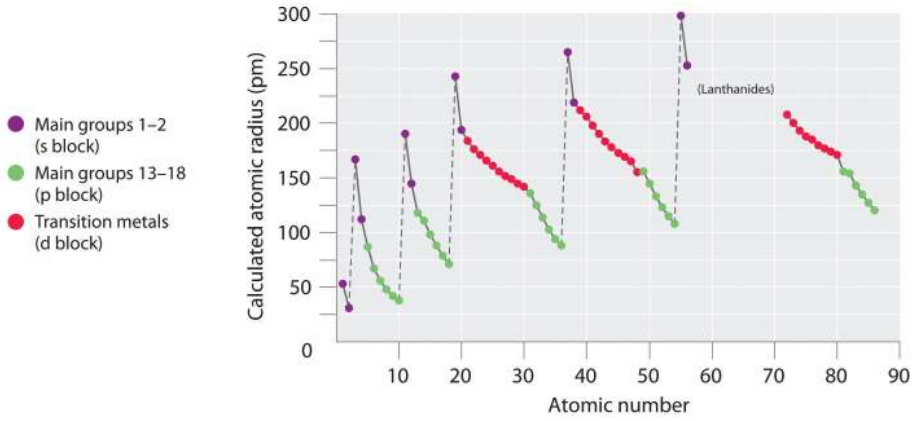


Figure 2.5.1: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

The melting point is a metric of the energy required to transform the solid phase of a substance into a liquid. Generally, the stronger the bond between the atoms of an element, the more energy required to break that bond. The melting points exhibit comparable, albeit more complex, periodic trends as observed in the atomic radii (Figure 2.5.2). Key feature of these trends are:

- Metals generally possess a *high melting point*.
- Most non-metals possess *low melting points*.
- The non-metal carbon possesses *the highest melting point of all the elements*. The semi-metal boron also possesses a high melting point.

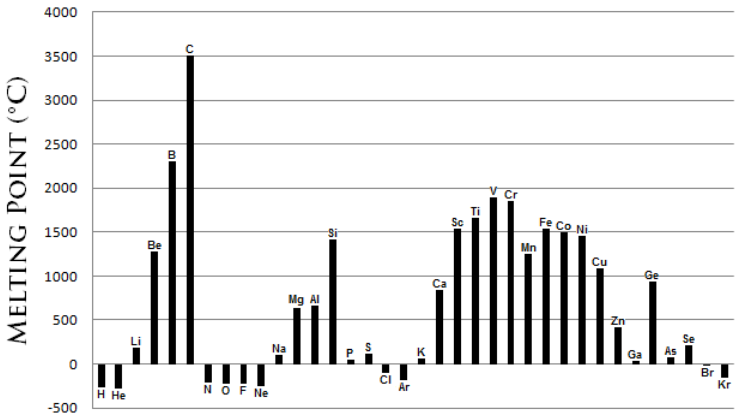


Figure 2.5.2: A plot of melting point vs. atomic number show a periodic trend.

The trends of the atomic radii and melting points (and other chemical and physical properties of the elements) can be explained by the electron shell theory of the atom discussed in the following sections.

Element Characteristics By Group

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

- **Group 1: The Alkali Metals –** lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr) are soft, shiny, and highly reactive metals. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively. *Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal.*
- **Group 2: The Alkaline Earth Metals –** beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra) are shiny, slivery-white, somewhat reactive metals. Beryllium, strontium, and barium are rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.
- **Group 17: The Halogens –** fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At) are nonmetals. The name halogen is derived from the Greek words for "salt forming," which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).
- **Group 18: The Noble Gases –** helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are gases at room temperature and pressure. Because the noble gases are composed of only single atoms, they are called monatomic. Because of their lack of reactivity, for many years they were called **inert gases** or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

To Your Health: Radon

Radon is an invisible, odorless noble gas that is slowly released from the ground, particularly from rocks and soils whose uranium content is high. Because it is a noble gas, radon is not chemically reactive. Unfortunately, it is radioactive, and increased exposure to it has been correlated with an increased lung cancer risk.

Because radon comes from the ground, we cannot avoid it entirely. Moreover, because it is denser than air, radon tends to accumulate in basements, which if improperly ventilated can be hazardous to a building's inhabitants. Fortunately, specialized ventilation minimizes the amount of radon that might collect. Special fan-and-vent systems are available that draw air from below the basement floor, before it can enter the living space, and vent it above the roof of a house.

After smoking, radon is thought to be the second-biggest *preventable* cause of lung cancer in the United States. The American Cancer Society estimates that 10% of all lung cancers are related to radon exposure. There is uncertainty regarding what levels of exposure cause cancer, as well as what the exact causal agent might be (either radon or one of its breakdown products, many of which are also radioactive and, unlike radon, not gases). The US Environmental Protection Agency recommends testing every floor below the third floor for radon levels to guard against long-term health effects.

Example 2.5.1: Groups

Provide the family/group names and period numbers (horizontal values) of each element.

a. Li
b. Ar
c. Ra

Solution:

a. Lithium is an alkali metal. It is located in period two.
b. Argon is a noble gas. It is located in period three.
c. Radium is an alkaline metal. It is located in period seven.

Example 2.5.2: Classification of Elements

Provide elemental names for the following combinations:

a. The alkali metal in period three.
b. The halogen in period two
c. A metalloid in period four
d. A transition metal in period three

Solution:

a. Sodium
b. Fluorine
c. Germanium or Arsenic
d. There are no transition metals in period three (gotcha!)

Key Takeaways

- The chemical elements are arranged in a chart called the periodic table.
- Some characteristics of the elements are related to their position on the periodic table.
- The number of valence electrons of an element can be determined by the group (vertical column) number in the Periodic Table. Elements with the same number of valence electrons have similar chemical properties.

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2.6: Electronic Structure of Atoms

Learning Objectives

- Describe how electrons are grouped within atoms into shells, subshells, and orbitals using quantum numbers.

You now know that the periodic table is arranged in groups and periods (columns and rows) based on chemical and physical properties of the different elements. The first element, hydrogen (Z=1) has one proton and one electron and as you move right across the rows, each subsequent element has one additional proton and electron. You may have asked yourself, why are periodic trends observed across the rows and down the groups? Or, why do the rows have different numbers of elements, giving the table a unique shape?

These questions can be answered by learning more about the electrons in atoms. Although we have discussed the general arrangement of subatomic particles in atoms, we have said little about how electrons occupy the space around the nucleus. Do they move around the nucleus at random, or do they exist in some ordered arrangement?

In 1913, the Danish scientist Niels Bohr suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number n (now called a **quantum number**). Bohr suggested that the energy of the electron in hydrogen was **quantized** because it was in a specific orbit; much like the steps on a staircase does not have half or quarter stairs or the keys on a piano don't have notes in between, there are no energy levels in between each orbit. Figure 2.6.1 shows a model of the hydrogen atom based on Bohr's ideas.

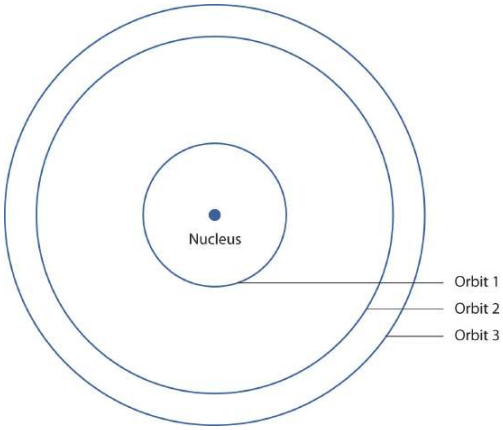


Figure 2.6.1: Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

Bohr's ideas were useful, but were applicable only to the hydrogen atom. However, later researchers generalized Bohr's ideas into a new theory called **quantum mechanics**, which explains the behavior of electrons as if they were acting as a wave, not as particles. Quantum mechanics predicts two major things: quantized energies for electrons of all atoms (not just hydrogen) and an organization of electrons within atoms. Electrons are no longer thought of as being randomly distributed around a nucleus or restricted to certain orbits (in that regard, Bohr was wrong). Instead, electrons are collected into groups (*shells*) and subgroups (*subshells*) that explain much about the chemical behavior of the atom.

In the quantum-mechanical model of an atom, which is the modern and currently accepted model, the location of electrons in the atom are described by four **quantum numbers**, not just the one predicted by Bohr. Much like your home address can be used to locate you in a specific state, city, street, and house number, the first three quantum numbers identify approximately where electrons are in an atom. The fourth quantum number describes the electron and whether it is spin up or down (clockwise or counterclockwise). The theory and mathematics behind these four quantum numbers are well beyond the scope of this textbook, however, it is useful to learn some of the basics in order to understand how atoms behave and interact with (react) with other atoms.

Electron Arrangements: Shells, Subshells, and Orbitals

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**, labeled by type as *s*, *p*, *d*, or *f*. The first shell has only one subshell, *s*. The second shell has two subshells, *s* and *p;* the third shell has three subshells, *s*, *p*, and *d*, and the fourth shell has four subshells, *s*, *p*, *d*, and *f*. Within each subshell, electrons are arranged into different numbers of **orbitals**, an *s* subshell is made up of one *s* orbital, a *p* subshell has two *p* orbitals, a *d* subshell, five *d* orbitals, and an *f* subshell, seven *f* orbitals. Each orbital has a different shape and orientation around the nucleus (Figure 2.6.1, however, rather than representing an orbit, as the name suggests, orbitals define a boundary for the region of space where a given electron is most likely to be found. Lastly, a single orbital can hold up to two electrons each with a different **spin**.

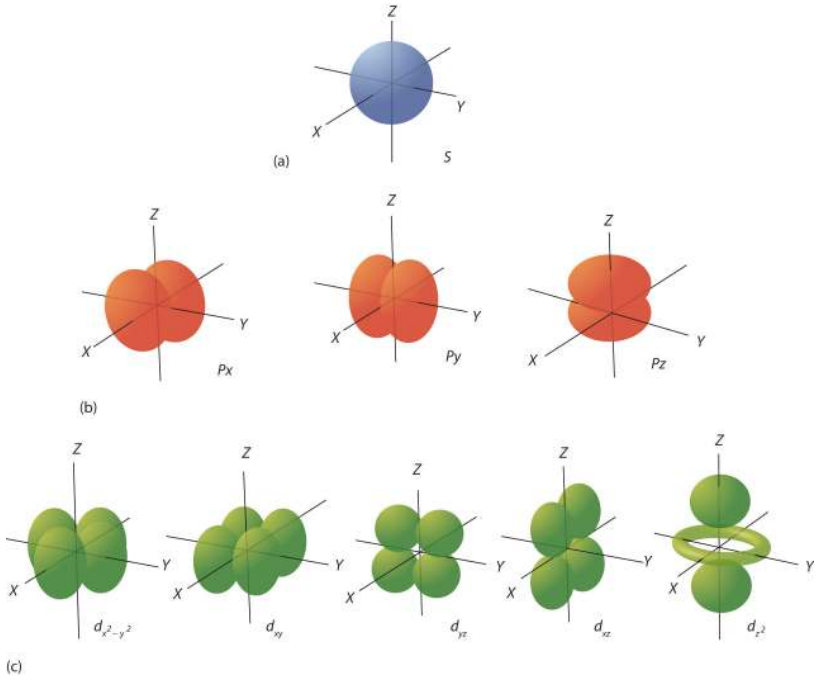


Figure 2.6.1: Electron Orbitals. (a) The lone *s* orbital in an *s* subshell is spherical in distribution. (b) The three *p* orbitals have two lobes, shaped kind of like dumbbells, each is oriented around the nucleus along a different axis. (c) The five *d* orbitals have four lobes, except for the d_{z^2} orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.

It is important to note that according to quantum theory, there are specific *allowed* combinations of quantum numbers and others that are not allowed. For example, shell two can only have two subshells, *s* with one orbital and *p* with 3 orbitals, therefore, this shell can hold a maximum of eight electrons (four orbitals times two electrons each). It takes practice to learn the allowed combinations as shown in Table 2.6.1 but it is helpful to visualize the atom as a sphere with the nucleus in the center. Close to the nucleus, there is a smaller amount of space for electrons – a smaller shell. As the number of electrons increases, the shells that hold the electrons get larger and thus further away from the nucleus.

Table 2.6.1: Shells and Subshells

Shell (*n*)	Number of Subshells	Names of Subshells	Number of Orbitals (*per Subshell*)	Number of Electrons (*per Subshell*)	Total Electrons (*per Shell*)
1	1	*1s*	1	2	2
2	2	*2s* and *2p*	1, 3	2, 6	8
3	3	*3s*, *3p*, and *3d*	1, 3, 5	2, 6, 10	18
4	4	*4s*, *4p*, *4d*, and *4f*	1, 3, 5, 7	2, 6, 10, 14	32

All of this information about the shell, subshell, and orbital is put together to make up the "address" for an electron and all of the addresses for all the electrons in an atom make up the **electron configuration**, which is described more later.

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2.7: Electron Configurations

Learning Objectives

- Describe how electrons are arranged in an atom using electron configurations.

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

We use numbers to indicate which shell an electron is in. 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 $\mathbf{1}\boldsymbol{s}^{\mathbf{1}}$ (spoken as “one-ess-one”) to describe the electron arrangement or distribution of electrons in hydrogen. This structure is called an **electron configuration** and is unique to hydrogen.

Helium atoms have 2 electrons. Both electrons fit into the 1*s* subshell because *s* subshells contain one *s* orbital which can hold up to 2 electrons; therefore, the electron configuration for helium atoms is $\mathbf{1}\boldsymbol{s}^{\mathbf{2}}$ (spoken as “one-ess-two”).

The 1*s* subshell can hold a maximum of 2 electrons, so the electron configuration for a lithium atom, which has three electrons, cannot be $1s^3$. Two of the lithium electrons can fit into the 1*s* subshell, but the third electron must go into the second shell and the lower energy orbital, which is the 2*s* orbital. Therefore, we write the electron configuration of a lithium atom as $\mathbf{1}\boldsymbol{s}^{\mathbf{2}}\mathbf{2}\boldsymbol{s}^{\mathbf{1}}$ (spoken as “one-ess-two two-ess-one”).

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 **1*s***, while the outermost shell (**2*s***) has 1 electron.

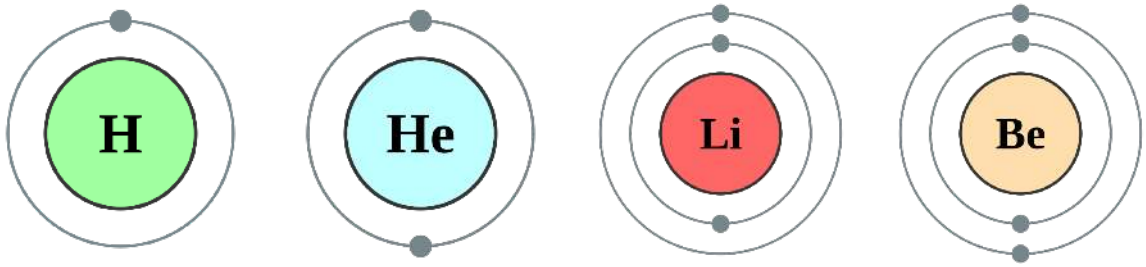


Figure 2.7.1: Shell diagrams of hydrogen (H), helium (He), lithium (Li), and Berryellium (Be) atoms. (CC BY-SA 2.0 UK; Greg Robson modified by Pumbaa via Wikipedia)

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**.

- **Rule 1 (Aufbau Principle):** Electrons occupy the lowest-energy orbitals (closest to the nucleus) possible, starting with 1*s*, then 2*s*, 2*p*, and continuing on to higher energy (further away from the nucleus). Shells increase in energy in order from 1 to 2 to 3, and so on. Within these shells, an *s* subshell is the lowest energy followed by *p*, then *d*, then *f*.
- **Rule 2 (Hund's Rule):** When electrons occupy degenerate orbitals (i.e. same shell and subshell), they must first singly occupy (half-fill) each empty orbital in a subshell before double occupying (completely filling) them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all spin up or all spin down). For example, all three *p* orbitals in a *p* subshell will have one electron before a single *p* orbital contains two electrons.
- **Rule 3 (Pauli-Exclusion Principle):** Each electron is described with a unique set of four quantum numbers (a unique address). Therefore, if two electrons occupy the same orbital, they must have different spins. This is the reason all orbitals can hold a maximum of two electrons.

Continuing on the periodic table to the next largest atom, beryllium, with 4 electrons, the electron configuration is $1s^2 2s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms, starting with boron, begin filling the 2*p* subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2p subshell:

- B: $1s^2 2s^2 2p^1$

- C: $1s^2 2s^2 2p^2$
- N: $1s^2 2s^2 2p^3$
- O: $1s^2 2s^2 2p^4$
- F: $1s^2 2s^2 2p^5$
- Ne: $1s^2 2s^2 2p^6$

At the end of the period the element neon, has filled the 2*s*, and 2*p* subshells, which completes the second shell. Now atoms with more electrons now must begin the third shell starting with the 3*s* subshell. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^2 2s^2 2p^6 3s^2 3p^1$. 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.

Table 2.7.1: Electron Configurations of the First 20 Elements

Atomic Number	Element Symbol	Outermost Shell	Electron 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] $4s^2$

Noble Gas Configuration

The electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$ (Table 2.7.1). 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 $[\mathrm{Ne}]$ for the $1s^2 2s^2 2p^6$ part of the configuration. Sodium's noble gas configuration becomes $[\mathrm{Ne}]\, 3s^1$.

The electron filling diagram shown below in Figure 2.7.2 is useful in remembering the order for electrons to occupy shells and subshells. Although it is much easier to use the periodic table as a guide for electron filling as you will see in the next section.

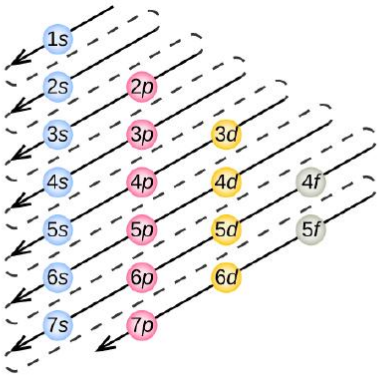


Figure 2.7.2: The order of electron filling in an atom. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

Example 2.7.1: 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 $1s^2 2s^2 2p^6 3s^2 3p^3$.

Exercise 2.7.1: 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 $1s^2 2s^2 2p^6 3s^2 3p^5$.

Orbital Diagrams

An **orbital diagram** is the more visual way to represent the arrangement of all the electrons in a particular atom. In an orbital diagram, the individual orbitals are shown as squares and orbitals within a sublevel are drawn next to each other horizontally. Each sublevel is labeled by its shell and sublevel. Electrons are indicated by arrows inside of the squares. An arrow pointing upwards indicates one spin direction, while a downward pointing arrow indicates the other direction. The orbital filling diagrams for hydrogen, helium, and lithium are shown in the figure below.

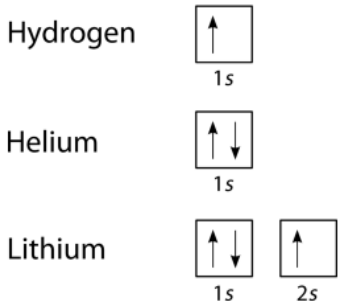


Figure 2.7.3: Orbital diagrams for hydrogen, helium, and lithium.

According to the Aufbau Principle, sublevels and orbitals are filled with electrons in order of increasing energy. Since the s sublevel consists of just one orbital, the second electron simply pairs up with the first electron as in helium. The next element is lithium and necessitates the use of the next available sublevel, the $2s$.

The orbital diagram for carbon is shown in Figure 2.7.10. There are two $2p$ electrons for carbon and each occupies its own $2p$ orbital (Hund's Rule).

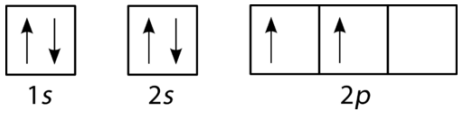


Figure 2.7.4: Orbital diagram for carbon.

Oxygen has four $2p$ electrons. After each $2p$ orbital has one electron in it, the fourth electron can be placed in the first $2p$ orbital with a spin opposite that of the other electron in that orbital.

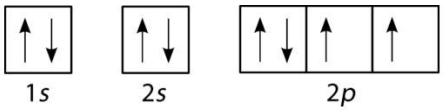


Figure 2.7.5: Orbital diagram for oxygen.

If you keep your papers in manila folders, you can pick up a folder and see how much it weighs. If you want to know how many different papers (articles, bank records, or whatever else you keep in a folder), you have to take everything out and count. A computer directory, on the other hand, tells you exactly how much you have in each file. We can get the same information on atoms. If we use an orbital filling diagram, we have to count arrows. When we look at electron configuration data, we simply add up the numbers.

Example 2.7.3: Carbon Atoms

Draw the orbital filling diagram for carbon and write its electron configuration.

Solution

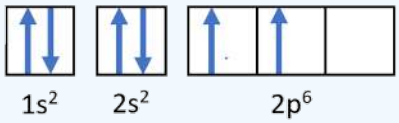
Step 1: List the known quantities and plan the problem.

Known

- Atomic number of carbon, Z=6

Use the order of fill diagram to draw an orbital filling diagram with a total of six electrons. Follow Hund's rule. Write the electron configuration.

Step 2: Construct the diagram.



Orbital filling diagram for carbon.

Electron configuration $1s^2 2s^2 2p^2$

Step 3: Think about your result.

Following the 2s sublevel is the 2p, and p sublevels always consist of three orbitals. All three orbitals need to be drawn even if one or more is unoccupied. According to Hund's rule, the sixth electron enters the second of those p orbitals and has the same spin as the fifth electron.

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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.

Remember, that the periodic table as a tool for organizing the known chemical elements(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. 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.*

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 2.8.1)

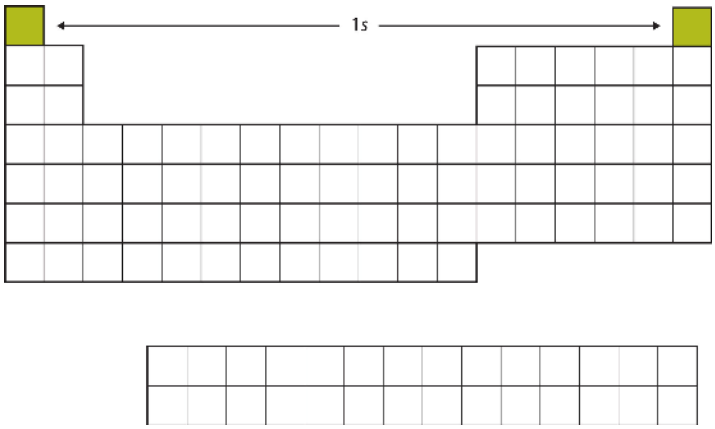


Figure 2.8.1: The 1*s* Subshell. H and He represent the filling of the 1*s* subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure 2.8.2 shows that these two elements are adjacent on the periodic table.

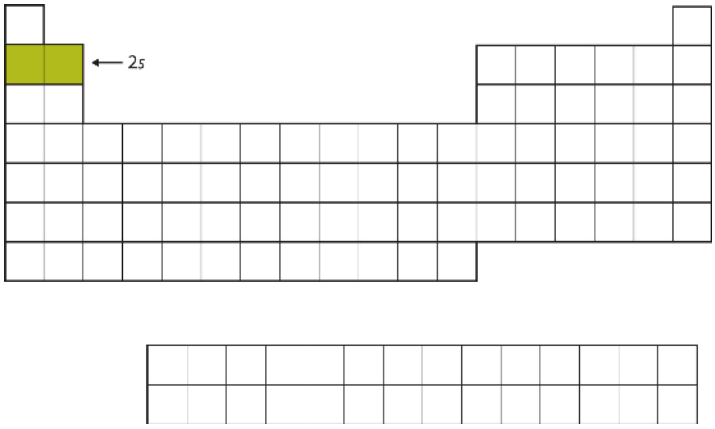


Figure 2.8.2: The 2*s* Subshell. In Li and Be, the 2*s* subshell is being filled.

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 2.8.3).

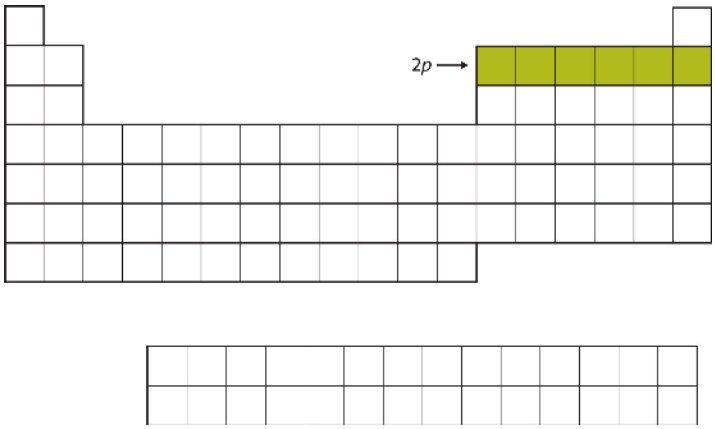


Figure 2.8.3: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

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 2.8.4).

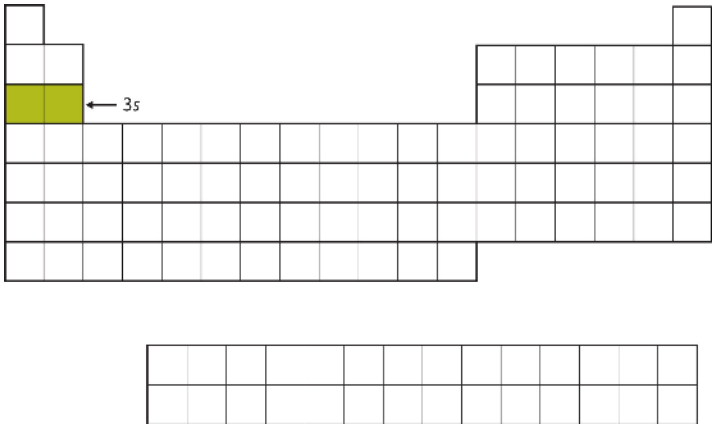


Figure 2.8.4: The 3*s* Subshell. Now the 3*s* subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 2.8.5).

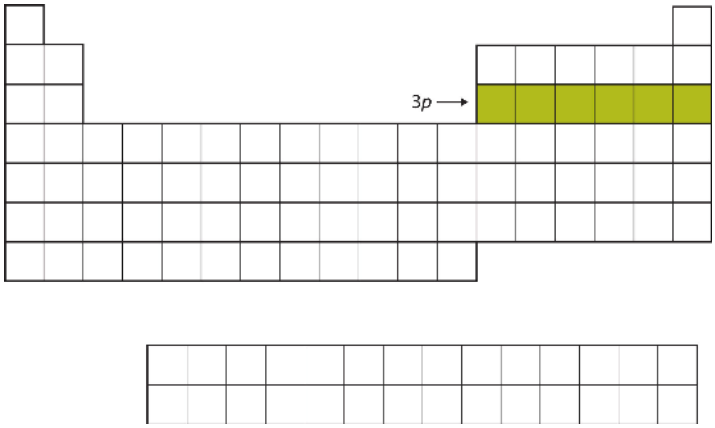


Figure 2.8.5: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 2.8.6).

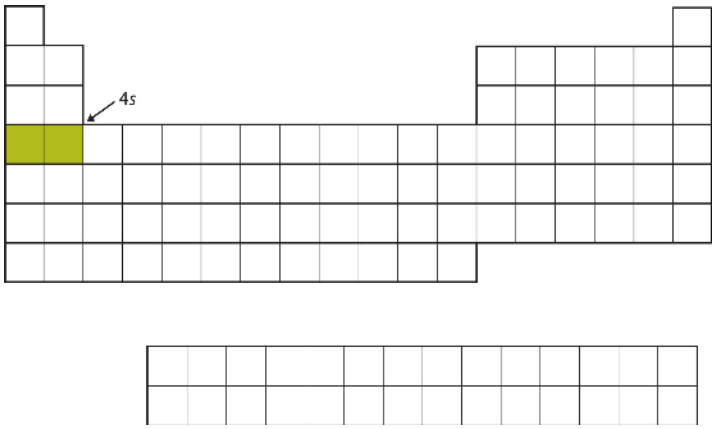


Figure 2.8.6: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

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 2.8.7).

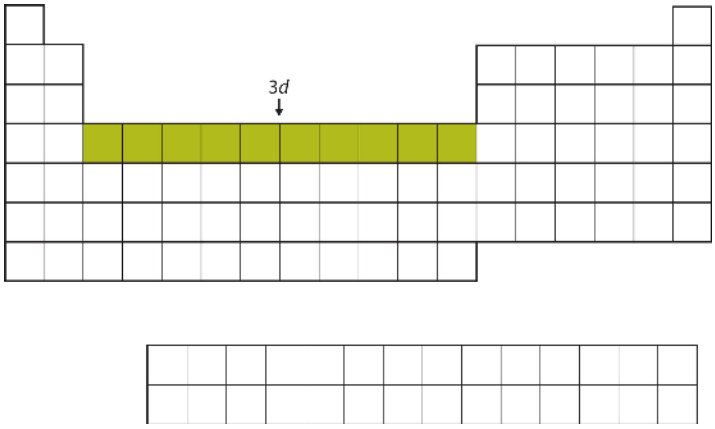


Figure 2.8.7: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

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

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 2.8.8 shows the blocks of the periodic table.

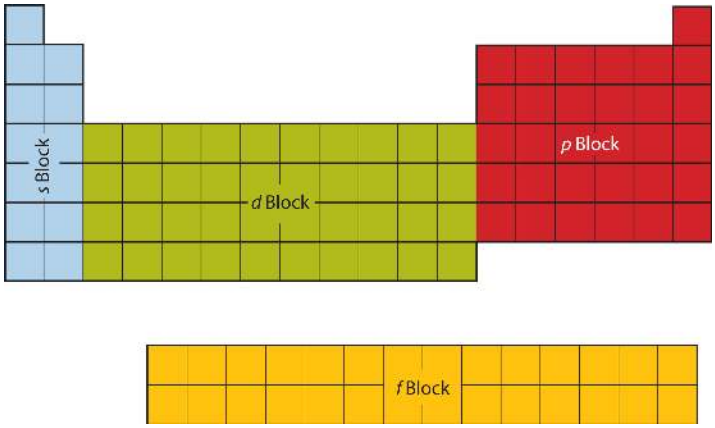


Figure 2.8.8: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

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:

Table shows first column of the periodic table and their electron configurations.

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 2.8.9. 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.

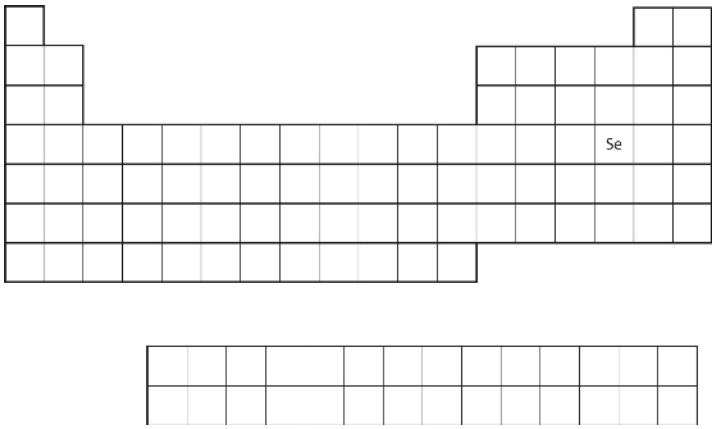


Figure 2.8.9: Selenium on the Periodic Table

Example 2.8.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure 2.8.10).

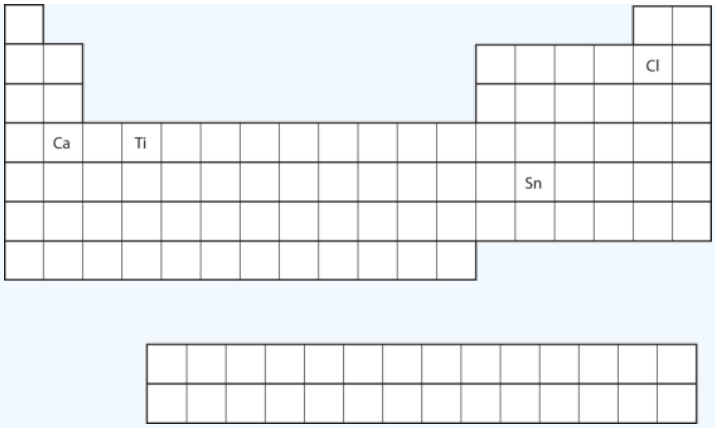


Figure 2.8.10: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

1. Ca is located in the second column of the *s* block. We would expect that its electron configuration should end with s^2. Calcium's electron configuration is $[Ar]4s^2$.
2. 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 2.8.10

a. Ti
b. Cl

Answer a

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

Answer b

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

Example 2.8.2: Aluminum

Write the electron configuration of neutral aluminum atom. The atomic number of Al is 13.

Solution

Aluminum has 13 electrons.

Start at Period 1 of the periodic table, Figure 2.8.2. Place two electrons in the 1s subshell ($\mathbf{1s^2}$).

Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell ($\mathbf{2s^2}$) and the next six electrons in the 2p subshell ($\mathbf{2p^6}$).

Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell ($\mathbf{3s^2}$) and the last one electron in the 3p subshell ($\mathbf{3p^1}$).

The electron configuration of Aluminum is $\mathbf{1s^22s^22p^63s^23p^1}$

? Exercise 2.8.2

Using Figure 2.8.2 as your guide, write the electron configuration of the atom that has 20 electrons

Answer

Start at Period 1 of Figure 2.8.2 Place two electrons in the 1s subshell (**$1s^2$**).

Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**$2s^2$**) and the next six electrons in the 2p subshell (**$2p^6$**).

Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**$3s^2$**) and the next six electron in the 3p subshell (**$3p^6$**).

Proceed to Period 4. Place the remaining two electrons in the 4s subshell (**$4s^2$).**

The electron configuration is **$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$**

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: Electron-Dot Symbols

Learning Objective

- Draw a Lewis electron dot symbol for a given atom.

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.

A **Lewis electron-dot symbol** (or electron-dot symbol or a Lewis symbol) 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. (It does not matter what order the positions are used.) For example, the electron-dot symbol for hydrogen is simply

$$\mathbf{H}\cdot \tag{2.9.1}$$

Because the side is not important, the electron-dot symbol could also be drawn as follows:

$$\dot{\mathbf{H}} \quad or \quad \cdot\mathbf{H} \quad or \quad \underset{\cdot}{\mathbf{H}} \tag{2.9.2}$$

The electron-dot symbol for helium, with two valence electrons, is as follows:

$$\mathbf{He:} \tag{2.9.3}$$

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:

$$\mathbf{Li}\cdot \tag{2.9.4}$$

Beryllium has two valence electrons in its 2*s* shell, so its eelectron-dot symbol is like that of helium:

$$\mathbf{Be:} \tag{2.9.5}$$

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:

$$\dot{\mathbf{B}}\mathbf{e:} \tag{2.9.6}$$

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 symbol for carbon is as follows:

$$\cdot\dot{\mathbf{C}}\mathbf{:} \tag{2.9.7}$$

With N, which has three *p* electrons, we put a single dot on each of the three remaining sides:

$$\cdot\underset{\cdot}{\dot{\mathbf{N}}}\mathbf{:} \tag{2.9.8}$$

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 a side has no more than two electrons.

$$\cdot\underset{\cdot}{\ddot{\mathbf{O}}}\mathbf{:} \tag{2.9.9}$$

Fluorine and neon have seven and eight dots, respectively:

$$\mathbf{:}\underset{\cdot}{\ddot{\mathbf{F}}}\mathbf{:} \tag{2.9.10}$$

$$:\ddot{\mathrm{N}}\mathrm{e}: \tag{2.9.11}$$

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 electron-dot symbol of atoms will never have more than eight dots around the atomic symbol.

Example 2.9.1:

What is the electron-dot symbol 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:

$$\dot{A}\dot{l}:$$

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:

$$\cdot\dot{\mathrm{S}}\mathrm{e}:$$

Exercise 2.9.1

What is the electron-dot symbol for each element?

a. phosphorus
b. argon

Answer

$$\cdot\dot{\mathrm{P}}:$$

$$:\ddot{\mathrm{A}}\mathrm{r}:$$

Summary

- Lewis electron-dot symbols use dots to represent valence electrons around an atomic symbol.

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CHAPTER OVERVIEW

3: Ionic Compounds

When you think of bonding, you may not think of ions or molecules. Like most of us, you probably think of bonding between people. Like people, molecules bond — and some bonds are stronger than others. It's hard to break up a mother and baby, or a molecule made up of one oxygen and two hydrogen atoms! A chemical bond is a force of attraction between atoms or ions. Bonds form when atoms share or transfer valence electrons. Valence electrons are the electrons in the outer energy level of an atom that may be involved in chemical interactions. Valence electrons are the basis of all chemical bonds.

3.1: Ions
3.2: Ions and the Octet Rule
3.3: Ions of Some Common Elements
3.4: Periodic Properties and Ion Formation
3.5: Naming Monoatomic Ions
3.6: Polyatomic Ions
3.7: Ionic Bonds
3.8: Formulas of Ionic Compounds
3.9: Naming Ionic Compounds
3.10: Some Properties of Ionic Compounds
3.11: H^+ and OH^- Ions - An Introduction to Acids and Bases

Thumbnail: The crystal structure of sodium chloride, NaCl, a typical ionic compound. The purple spheres represent sodium cations, Na^+, and the green spheres represent chloride anions, Cl^-. (Public Domain; Benjah-bmm27 via Wikipedia)

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3.1: Ions

Learning Objectives

- Describe how an ion is formed.
- Distinguish the difference between the two types of ions.

Ions

As introduced previously, 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 3.1.1).

Figure 3.1.1: A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. When it loses an electron, the resulting sodium cation has one more proton (11) than electrons (10), giving it an overall positive one charge, Na+.

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 3.1.2)

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

Figure 3.1.2: A chlorine atom (Cl) has equal numbers of protons and electrons (17) and is uncharged. When it gains an electron, the resulting chlorine anion has one more electron (18) than protons (17), giving it an overall negative one charge, Cl–.

Note Naming Ions

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.

Example 3.1.1

A calcium (Ca) atom loses two electrons and a sulfur (S) atom gains two electrons. Determine if the resulting ions are cations or anions? Write the ion symbols for each.

Solution

When calcium (Z = 20) gains two electrons the resulting ion will have 18 electrons and 20 protons and therefore a charge of +2 (there are two more positive protons than negative electrons), it is a cation. The symbol for a calcium ion is Ca^{2+}.

When sulfur (Z = 16) gains two electrons the resulting ion will have 18 electrons and 16 protons and therefore a charge of –2 (there are two more negative electrons than positive protons), it is an anion. The symbol for a sulf*ide* ion is $S^{2–}$.

Key Takeaways

- Ions are formed when atoms gain or lose electrons.
- Ions can be positively charged (cations) or negatively charged (anions).

Contributors

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3.2: Ions and the Octet Rule

Learning Objectives

- Use the octet rule and electron configurations to determine if an atom will gain or lose electrons forming anions or cations.

Ions are formed when an atom, usually on the left side of the periodic table, *reacts with* and *transfers* one or more electrons to another atom, usually on the right side of the periodic table. These electrons are usually *lost from* or *gained into* the **valence shell**, or outermost energy level (shell). Why do some atoms lose electrons and others gain electrons? How can we predict the number of electrons lost or gained? Which ions are stable and which ions do not form at all? These questions are best answered by looking at electron configurations and considering what is called the **octet rule**, which states that atoms gain or lose electrons to form a stable, noble gas configuration, i.e., a filled subshell containing *eight* electrons. Therefore, it is useful to take a closer 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 with eight valence electrons.

$$\begin{matrix} \mathrm{Na} & \rightarrow & \mathrm{Na^+ + e^-} \\ 1s^2\ 2s^2\ 2p^6\ 3s^1 & & 1s^2\ 2s^2\ 2p^6 \end{matrix} \tag{3.2.1}$$

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.

$$\begin{matrix} \mathrm{Cl + e^-} & \rightarrow & \mathrm{Cl^-} \\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5 & & 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 \end{matrix} \tag{3.2.2}$$

The octet rule and the periodic table can be used to predict what ions will form; main group elements on the left side of the periodic table (metals in groups 1, 2, and 13) tend to lose electrons (form cations) to achieve the same electron configuration as the noble gas just *before* them in the table. The number of electrons the atom will lose depends on what group the atom is in, i.e., how many valence electrons it has. Main group elements on the right side of the periodic table (nonmetals in groups 15-17) will gain electrons to achieve the same electron configuration as the noble gas just *after* them in the table. Again, the number of electrons the atom will gain depends on the number of valence electrons it has and how many are needed to reach the filled subshell, eight electrons.

Note Violation of the Octet Rule

It is *not impossible* to violate the octet rule. Consider sodium: in its elemental form, it has one valence electron and is stable. It is rather reactive, however, and does not require a lot of energy to remove that electron to make the Na^+ ion. We *could* remove another electron by adding even *more* energy to the ion, to make the Na^{2+} ion. However, that requires much more energy than is normally available in chemical reactions, so sodium stops at a 1+ charge after losing a single electron. It turns out that the Na^+ ion has a complete octet in its new valence shell, the $n = 2$ shell, which satisfies the octet rule. The octet rule is a result of trends in energies and is useful in explaining why atoms form the ions that they do.

Example 3.2.1

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? Write the symbol and the electron configuration for an aluminum ion.

Solution

The electron configuration of Al atom is $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum has three valence electrons in the third energy level, ($3s^2 3p^1$). The cation, Al^{3+}, is formed when these three valence electrons are **lost**, leaving the configuration for the noble gas neon, $1s^2 2s^2 2p^6$.

? Exercise 3.2.1

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? Write the symbol and electron configuration for oxide ion.

Answer

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

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3.3: 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 3.3.1 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 3.3.1 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}.

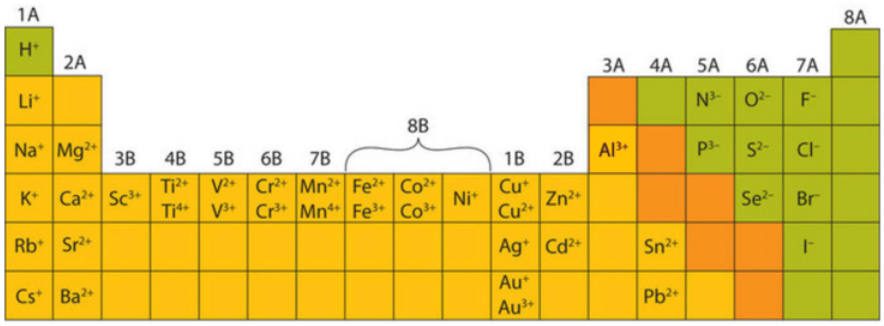


Figure 3.3.1: Common ions formed by specific elements on the periodic table. The charge that a representative (main group element) acquires when it becomes an ion is related to the location on the periodic table. Note that some metal atoms, specifically the transition elements, commonly form ions with variable charges.

mple

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.

rcise

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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3.4: Periodic Properties and Ion Formation

Learning Objectives

- Describe ionization energy and electron affinity and how this relates to ion formation trends.

We have seen that elements often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. Why is this so? In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energy

Because atoms do not spontaneously lose electrons, energy is *required* to remove an electron from an atom to form a cation. Chemists define the ionization energy (IE) of an element as the amount of energy needed to remove an electron from the gaseous atom A in its ground state. IE is therefore the energy required for the reaction:

$$A(g) \rightarrow A^{+}(g) + e^{-} \qquad \text{energy required=IE} \tag{3.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($IE > 0$) for the reaction as written in Equation 3.4.1. Larger values of (IE) mean that the electron is more tightly bound to the atom and thus, harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol \tag{3.4.2}$$

As you move *across* a row on the periodic table, the ionization energies generally tend to increase. This means that elements on the left side of the periodic table lose electrons more easily (requires less energy to remove an electron) than those on the right side of the periodic table. The trend in ionization energy can be explained by considering the trend in atomic radius (explained in an earlier chapter). As you move from left to right on the periodic table, the atomic size decreases and the electrostatic interactions between the nucleus and valence electrons increases, which increases the energy required to remove electrons, thus the (IE) increases.

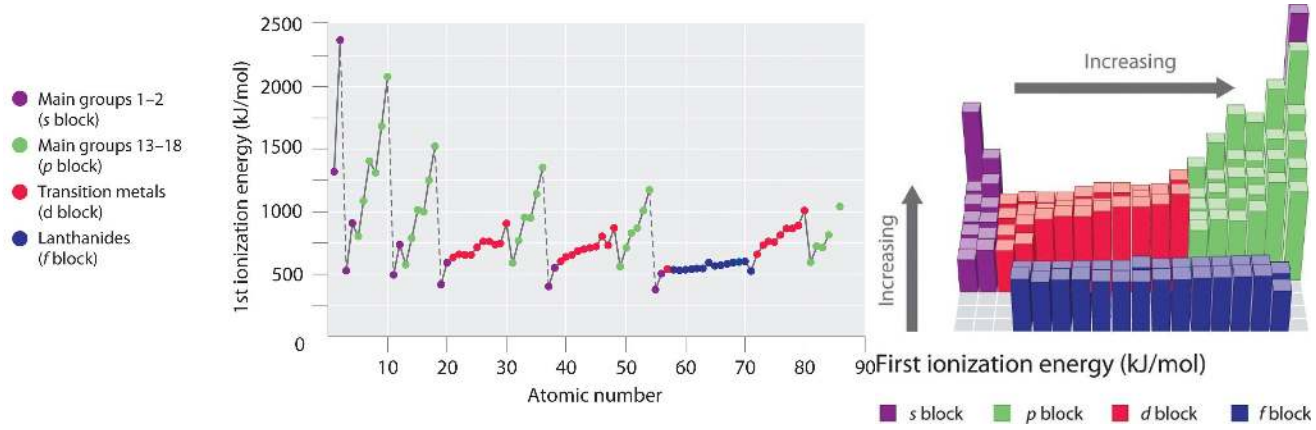


Figure 3.4.1: Ionization Energy Trends on the Periodic Table. (Left Figure) A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18). (Right Figure) First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements

If you look closely at the trends in ionization energy, you will notice that there are some "exceptions" where you see a decrease in energy rather than an increase. In periods 1 and 2, you can see this decrease in (IE) between groups 2 and 3 and again between groups 5 and 6. These variations in the trend can be further explained by looking closely at the electron configurations of the atoms in question. As you move from magnesium to aluminum, one electron is added to the 3*p* subshell. This 3*p* electron is slightly further from the nucleus (higher in energy) and is therefore, more easy to remove compared to the 3*s* electrons. The decrease between phosphorous and sulfur occurs because the added electron in sulfur is the first to be paired in the *p* subshell. These two electrons in the same *p* orbital repel each other, making the sulfur atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements. This electron is easier to remove because it will lead to more stability.

Example 3.4.1: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise 3.4.1: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer

As

Electron Affinity

The electron affinity (EA) of an element A is defined as the energy change that occurs when an electron is added to a gaseous atom or ion:

$$A(g) + e^- \rightarrow A^-(g) \qquad \text{energy change} = EA \tag{3.4.3}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released (Figure 3.4.2).

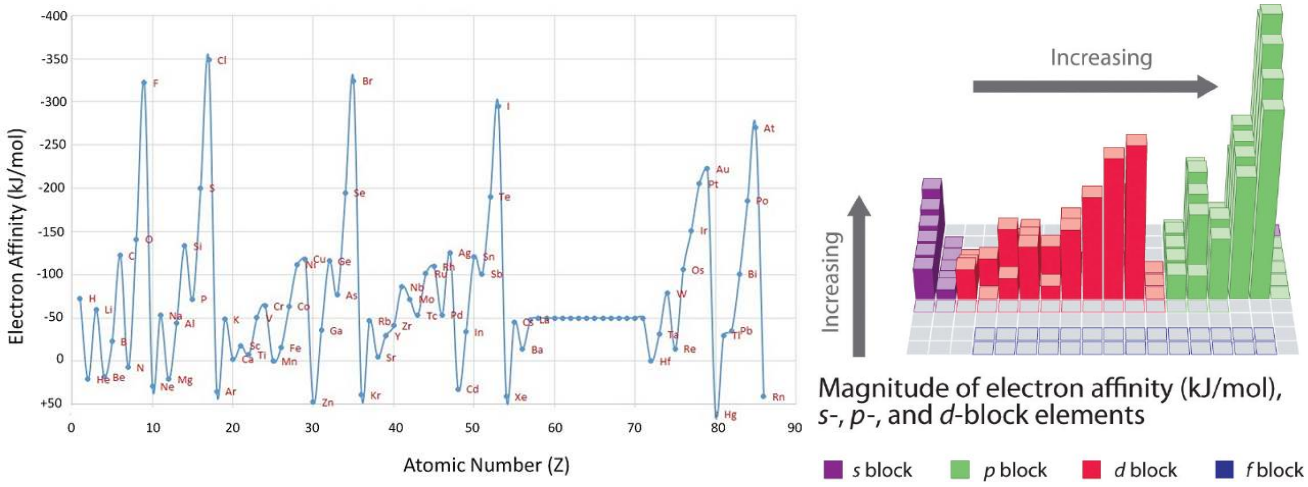


Figure 3.4.2: Electron Affinity Trends. (Left) A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies). (Right) Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$\mathrm{Cl(g) + e^- \rightarrow Cl^-(g)} \qquad EA = -346\ kJ/mol \tag{3.4.4}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be(g) + e^- \rightarrow Be^-(g)} \qquad EA \geq 0 \tag{3.4.5}$$

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as the energy level increases, the extra electrons enter orbitals that are increasingly far from the nucleus, and it is less easy to gain extra electrons forming anions.

Example 3.4.2: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 3.4.2: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer

Rb

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3.5: Naming Monoatomic Ions

Learning Objectives

- Name monoatomic ions using the defined nomenclature rules.

After learning a few more details about the names of individual ions, you will be a step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

Naming Cations

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. Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different ionic 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*.

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 3.5.1 lists the elements that use the common system, along with their respective cation names.

Table 3.5.1: Names of Some Cations

Element	Charge	Symbol	Common System Name	Stock System Name
chromium	2+	Cr^{2+}	chrom*ous* ion	chromium(II) ion
	3+	Cr^{3+}	chrom*ic* ion	chromium(III) ion
copper	1+	Cu^+	cupr*ous* ion	copper(I) ion
	2+	Cu^{2+}	cupr*ic* ion	copper(II) ion
iron	2+	Fe^{2+}	ferr*ous* ion	iron(II) ion
	3+	Fe^{3+}	ferr*ic* ion	iron(III) ion
lead	2+	Pb^{2+}	plumb*ous* ion	lead(II) ion
	4+	Pb^{3+}	plumb*ic* ion	lead(IV) ion
tin	2+	Sn^{2+}	stann*ous* ion	tin(II) ion
	4+	Sn^{4+}	stann*ic* ion	tin(IV) ion

Naming Anions

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 3.5.2 lists the names of some common monatomic ions.

Table 3.5.2: Some Monatomic Anions

Element	Charge	Symbol	Name
fluorine	1–	F^-	fluoride ion
chlorine	1–	Cl^-	chloride ion
bromine	1–	Br^-	bromide ion
iodine	1–	I^-	iodide ion
oxygen	2–	O^{2-}	oxide ion
sulfur	2–	S^{2-}	sulfide ion
phosphorous	3–	P^{3-}	phosphide ion
nitrogen	3–	N^{3-}	nitride ion

Example 3.5.1

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. SO_3^{2-}
d. NH_4^+
e. Cu^+

Answer a

the calcium ion

Answer b

the sulfide ion (from Table 3.5.2)

Answer c

the sulfite ion

Answer d

the ammonium ion

Answer e

the copper(I) ion or the cuprous ion (copper can form cations with either a 1+ or 2+ charge, so we have to specify which charge this ion has

Exercise 3.5.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. SO_4^{2-}
d. Ba^{2+}
e. HCO_3^-

Answer a

the iron (II) or ferrous ion

Answer b

the iron (III) or ferric ion

Answer c

the sulfate ion

Answer d

the barium ion

Answer e

the bicarbonate ion or hydrogen carbonate ion

Example 3.5.2

Write the formula for each ion.

a. the bromide ion
b. the phosphate ion
c. the cupric ion
d. the magnesium ion

Answer a

Br^-

Answer b

PO_4^{3-}

Answer c

Cu^{2+}

Answer d

Mg^{2+}

Exercise 3.5.2

Write the formula for each ion.

a. the fluoride ion
b. the carbonate ion
c. the ferrous ion
d. the potassium ion

Answer a

F^-

Answer b

CO_3^{2-}

Answer c

Fe^{2+}

Answer d

K^+

Note Chemistry Is Everywhere: Salt

The element sodium (part [a] in the accompanying figure) is a very reactive metal; given the opportunity, it will react with the sweat on your hands and form sodium hydroxide, which is a very corrosive substance. The element chlorine (part [b] in the

accompanying figure) is a pale yellow, corrosive gas that should not be inhaled due to its poisonous nature. Bring these two hazardous substances together, however, and they react to make the ionic compound sodium chloride (part [c] in the accompanying figure), known simply as salt.

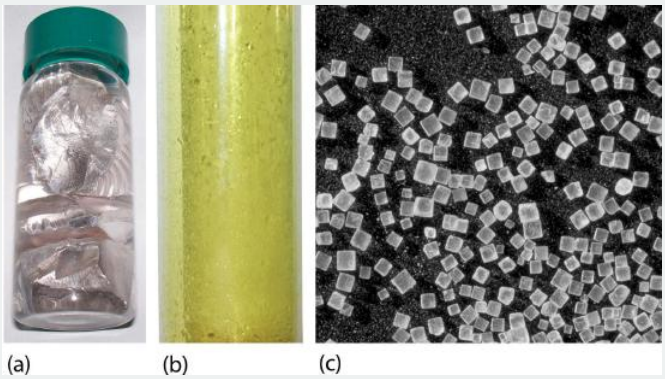


Figure 3.5.1: Sodium + Chlorine = Sodium Chloride (a) Sodium is a very reactive metal. (b) Chlorine is a pale yellow, noxious gas. (c) Together, sodium and chlorine make sodium chloride-salt-which is necessary for our survival. Source: Photo(opens in new window) on the left courtesy of Greenhorn1. Photo(opens in new window) in the center courtesy of Benjah-bmm27, . Photo on the right © Thinkstock.

Salt is necessary for life. Na^+ ions are one of the main ions in the human body and are necessary to regulate the fluid balance in the body. Cl^- ions are necessary for proper nerve function and respiration. Both of these ions are supplied by salt. The taste of salt is one of the fundamental tastes; salt is probably the most ancient flavoring known, and one of the few rocks we eat.

The health effects of too much salt are still under debate, although a 2010 report by the US Department of Agriculture concluded that "excessive sodium intake…raises blood pressure, a well-accepted and extraordinarily common risk factor for stroke, coronary heart disease, and kidney disease."US Department of Agriculture Committee for Nutrition Policy and Promotion, Report of the Dietary Guidelines Advisory Committee on the Dietary Guidelines for Americans, accessed January 5, 2010. It is clear that most people ingest more salt than their bodies need, and most nutritionists recommend curbing salt intake. Curiously, people who suffer from low salt (called *hyponatria*) do so not because they ingest too little salt but because they drink too much water. Endurance athletes and others involved in extended strenuous exercise need to watch their water intake so their body's salt content is not diluted to dangerous levels.

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3.6: 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.

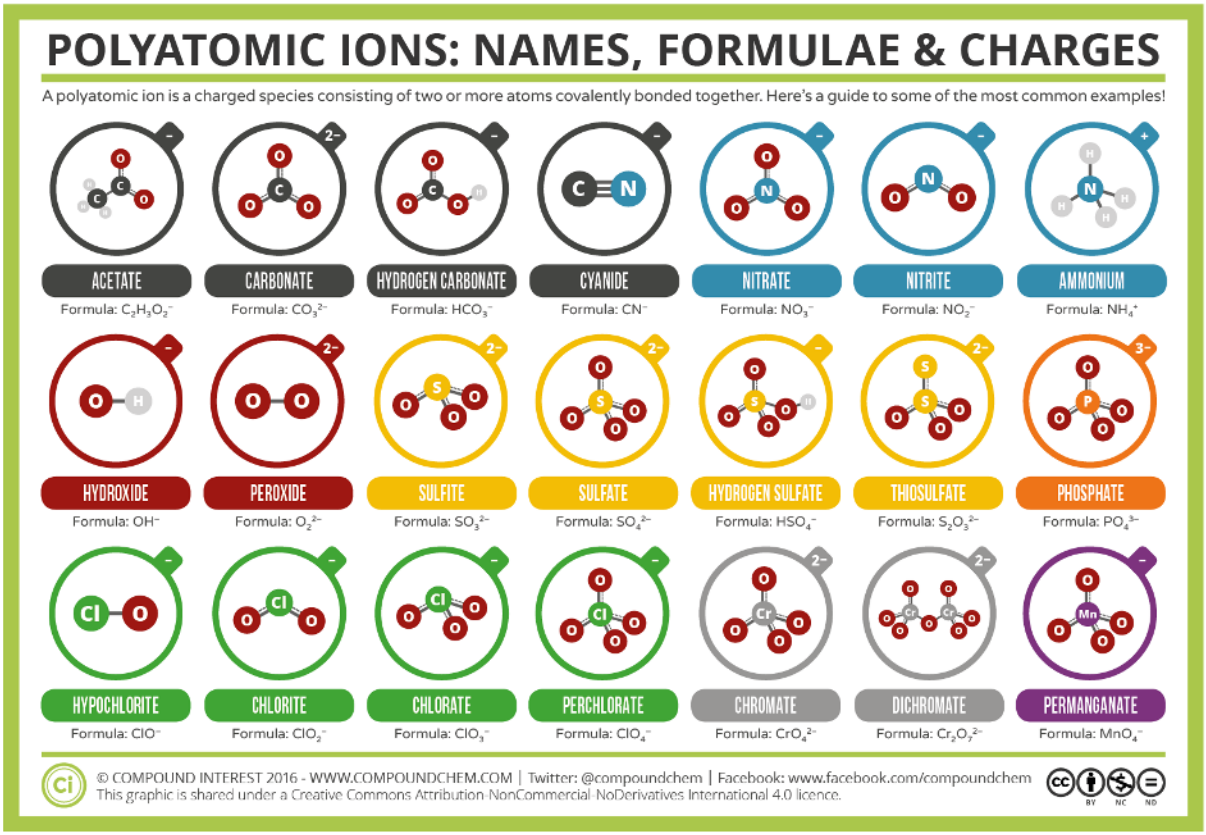


Figure 3.6.1: Polyatomic Ions Infographic

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table 3.6.1 lists the ion names and ion formulas of the most common polyatomic ions. 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: 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^-

Ion Name	Ion Formula
acetate ion	$C_2H_3O_2^-$ **or** $CH_3CO_2^-$
nitrate ion	NO_3^-
nitrite ion	NO_2^-
sulfate ion	SO_4^{2-}
sulfite ion	SO_3^{2-}
phosphate ion	PO_4^{3-}
phosphite 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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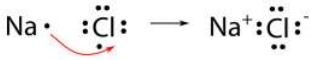
3.7: Ionic Bonds

Learning Objectives

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

Oppositely charged particles attract each other. This attractive force is often referred to as an **electrostatic attraction**. An **ionic bond** is the electrostatic electrostatic attraction 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 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 3.7.1). In other words, each ion is attracted to many of its neighboring ions forming a sodium chloride crystal or **ionic solid**.

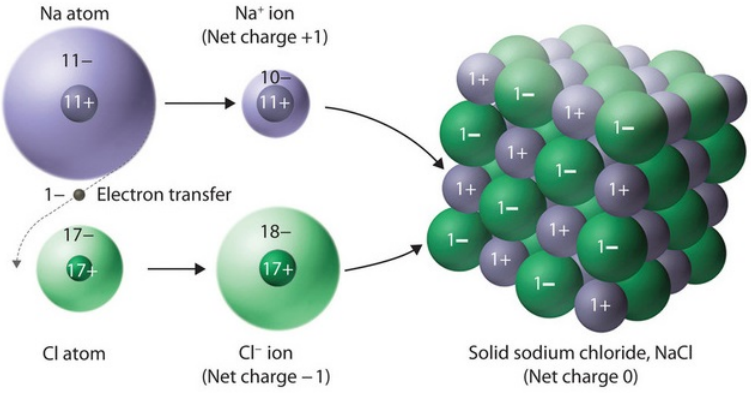


Figure 3.7.1: Ionic Bonding. The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting Na^+ and Cl^- ions form a three-dimensional solid that is held together by attractive electrostatic interactions.

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3.8: Formulas of Ionic Compounds

Learning Objectives

- Write the chemical formula for a simple ionic compound based on the charges of the cations and anions in the compound.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Ionic Compounds Formed From Monoatomic Ions

Consider an Na atom in the presence of a Cl atom. The two atoms have these Lewis electron dot diagrams and electron configurations:

$$\mathbf{Na}\cdot \qquad \cdot\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}$$

$$[Ne]\,3s^1 \qquad [Ne]\,3s^2 3p^5$$

For the Na atom to obtain an octet, it must lose an electron; for the Cl atom to obtain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

$$\mathbf{Na}\cdot \curvearrowright \cdot\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}$$

resulting in two ions—the Na^+ ion and the Cl^- ion:

$$\mathbf{Na}\cdot^{+} \qquad \mathbf{:}\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}^{-}$$

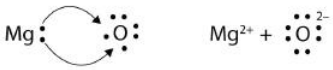
$$[Ne] \qquad [Ne]\,3s^2 3p^6$$

Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na^+ and Cl^- ions:

$$\mathbf{Na}\cdot^{+} + \mathbf{:}\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}^{-} \rightarrow Na^+Cl^- \;\; or \;\; NaCl$$

where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. As explained previously, the attraction between oppositely charged ions is called an **ionic bond**.

In electron transfer, the number of electrons lost must equal the number of electrons gained. We saw this in the formation of NaCl. A similar process occurs between Mg atoms and O atoms, except in this case two electrons are transferred:



Magnesium donates two electrons to oxygen to empty its own orbital and fill oxygens, thus creating Mg2+ and O2-.

The two ions each have octets as their valence shell, and the two oppositely charged particles attract, making an ionic bond:

$$\mathbf{Mg}^{2+} + \mathbf{:}\ddot{\underset{\cdot\,\cdot}{\mathbf{O}}}\mathbf{:}^{2-} \qquad Mg^{2+}O^{2-} \; or \; MgO$$

What about when an Na atom interacts with an O atom? The O atom needs two electrons to complete its valence octet, but the Na atom supplies only one electron:

$$\mathbf{Na}\cdot \curvearrowright \cdot\ddot{\underset{\cdot}{\mathbf{O}}}\mathbf{:}$$

The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:



Two sodium atoms donate one electron each to oxygen to empty their orbitals and fill oxygen's, thus creating 2 Na+ and O2-.

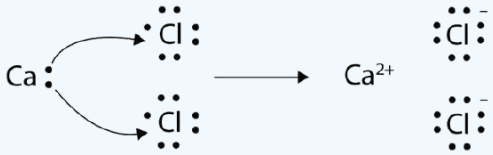
These three ions attract each other to form an overall neutrally charged ionic compound, which we write as Na_2O. The need for the number of electrons lost to be equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is also required by the law of conservation of matter.

3.8.1 Example

With arrows, illustrate the transfer of electrons to form calcium chloride from Ca atoms and Cl atoms.

Solution

A Ca atom has two valence electrons, while a Cl atom has seven electrons. A Cl atom needs only one more to complete its octet, while Ca atoms have two electrons to lose. We need two Cl atoms to accept the two electrons from one Ca atom. The transfer process is as follows:



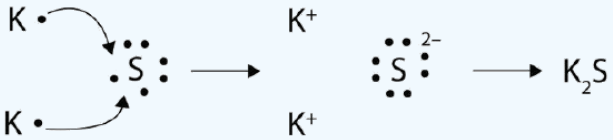
Calcium donates two electrons, one each going to a chlorine. This empties calcium's orbital and fills both of the chlorines'. This creates Ca2+ and two Cl-.

The oppositely charged ions attract one another to make $CaCl_2$.

3.8.1 Exercise

With arrows, illustrate the transfer of electrons to form potassium sulfide from K atoms and S atoms.

Answer



Two potassium atoms donate an electron to sulphur to fill sulphur's orbital and empty their own, thus creating two K+ and one S2-. They ionically bond to form K2S.

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.

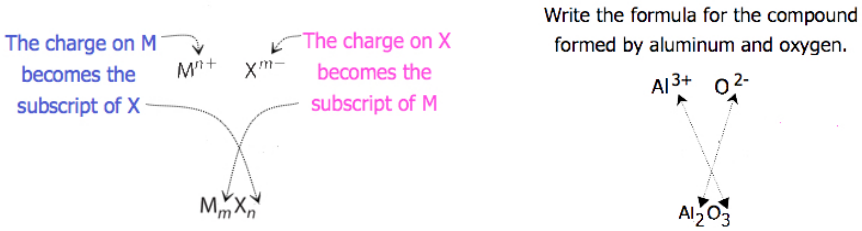


Figure 3.8.1: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

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 **PbO_2**. The empirical formula has one Pb^{4+} ion and two O^{2-} ions.

Example 3.8.2: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 3.8.2) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Figure 3.8.2: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

Exercise 3.8.2

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Ionic Compounds Formed From Polyatomic Ions

Many ionic compounds contain polyatomic ions as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate $\left(PO_4^{3-}\right)$ groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 3.8.3: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4^-$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Exercise 3.8.3

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 $C_2H_3O_2^-$ = $Al(C_2H_3O_2)_3$

Formula Unit

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 3.8.3). 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 or *simplest formula*, 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 3.8.3 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

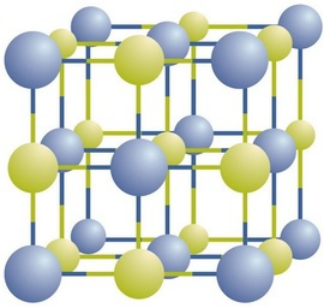


Figure 3.8.3: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

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3.9: Naming Ionic Compounds

Learning Objectives

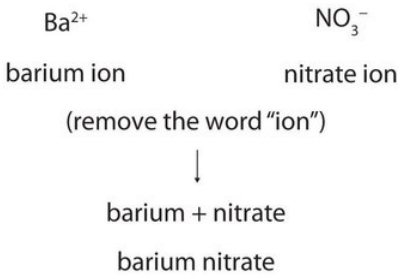
- Write the names for ionic compounds by recognizing and naming the ions in the formula unit.

Ionic compounds are named using the formula unit and by following some important conventions. First, the name of the cation is written *first* followed by the name of 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* included in the name (or the formula). Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. The proper formula for an ionic compound will show how many of each ion is needed to balance the total positive and negative charges; the name does not need to include indication of this ratio.

There are two main types of ionic compound with different naming rules for each; Type I: compounds containing cations of main group elements and Type II: compounds containing cations of variable charge (generally transition metals). Below we will look at examples of each type to learn the rules for naming.

Type I Ionic Compounds

Cations of main group elements do not have variable charges and are the simply named by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $\mathrm{Ba(NO_3)_2}$?



The compound's name does not need to indicate that there are two nitrate ions for every barium ion. You must determine the ratio of ions in the formula unit by balancing the positive and negative charges.

Type II Ionic Compounds

Some metals can form cations with variable charges. When naming 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 $\mathrm{FeCl_2}$ and $\mathrm{FeCl_3}$. In the first compound, the iron ion has a 2+ charge because there are two $\mathrm{Cl^-}$ 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 $\mathrm{Cl^-}$ 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. If we were to use the stems and suffixes of the *common system*, the names would be ferrous chloride and ferric chloride, respectively.

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 3.9.1. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 3.9.1: Everyday Ionic Compounds

Ionic Compound	Name	Use
NaCl	sodium chloride	ordinary table salt

KI	potassium iodide	added to “iodized” salt for thyroid health
NaF	sodium fluoride	ingredient in toothpaste
$NaHCO_3$	sodium bicarbonate	baking soda; used in cooking (and in antacids)
Na_2CO_3	sodium carbonate	washing soda; used in cleaning agents
NaOCl	sodium hypochlorite	active ingredient in household bleach
$CaCO_3$	calcium carbonate	ingredient in antacids
$Mg(OH)_2$	magnesium hydroxide	ingredient in antacids
$Al(OH)_3$	aluminum hydroxide	ingredient in antacids
NaOH	sodium hydroxide	lye; used as drain cleaner
K_3PO_4	potassium phosphate	food additive (many purposes)
$MgSO_4$	magnesium sulfate	added to purified water
Na_2HPO_4	sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3	sodium sulfite	preservative

As you practice naming compounds, use Figure 3.9.1 as a guide.

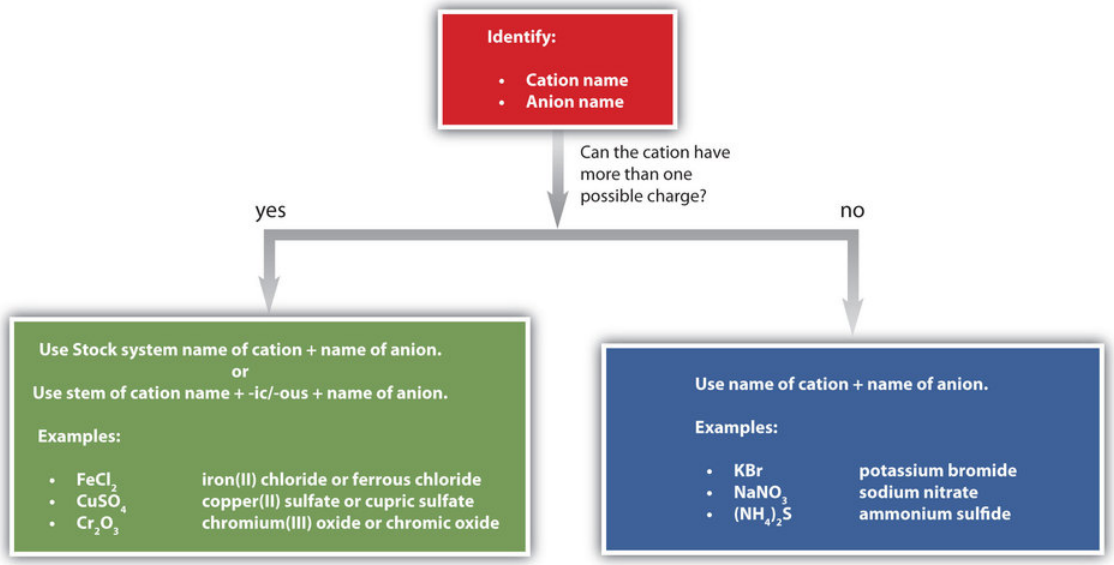


Figure 3.9.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

Identify the cation name and the anion name. If the cation can have more than one possible charge, either use the Stock system name of the cation and name of the anion, or use the stem of the cation name and -ic/-ous and the name of the anion. Examples of this would be FeCl2, which is iron(II) chloride of ferrous chloride, CuSO4, which is copper(II) sulfate or cupric sulfate, and Cr2O3, which is chromium(III) oxide or chromic oxide. If the cation can not have more than one possible charge, use the name of the cation and the name of the anion. Examples of this would be KBr, which is potassium bromide, NaNO3, which is sodium nitrate, and (NH4)2S, which is ammonium sulfide.

Example 3.9.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $Ca_3(PO_4)_2$
b. $(NH_4)_2Cr_2O_7$

c. KCl
d. CuCl
e. SnF_2

Answer a

calcium phosphate

Answer b

ammonium dichromate (the prefix *di-* is part of the name of the anion)

Answer c

potassium chloride

Answer d

copper(I) chloride or cuprous chloride

Answer e

tin(II) fluoride or stannous fluoride

? Exercise 3.9.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $ZnBr_2$
b. $Fe(NO_3)_3$
c. Al_2O_3
d. CuF_2
e. AgF

Answer a

zinc bromide

Answer b

iron (III) nitrate or ferric nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride or cupric fluoride

Answer e

silver fluoride

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3.10: 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.

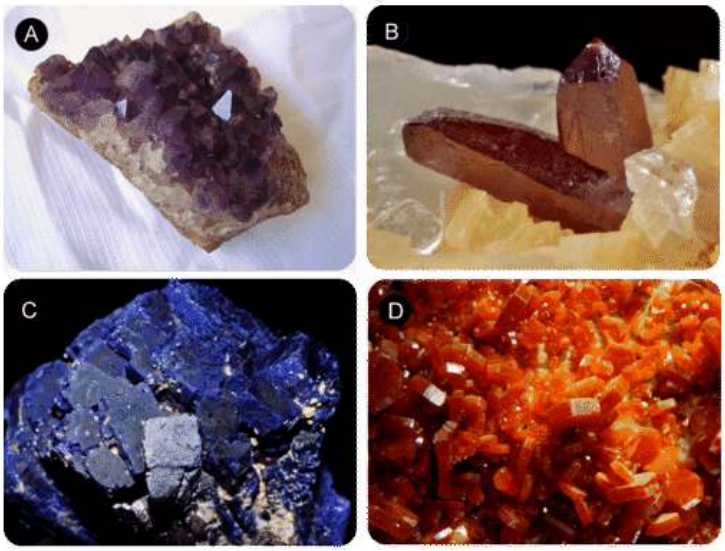


Figure 3.10.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz, SiO_2, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral, $Cu_3(CO_3)_2(OH)_2$. (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.

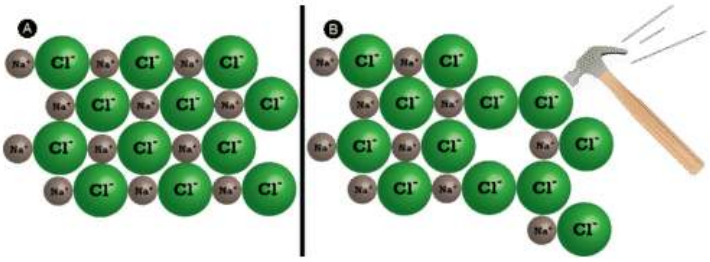


Figure 3.10.2: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

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.

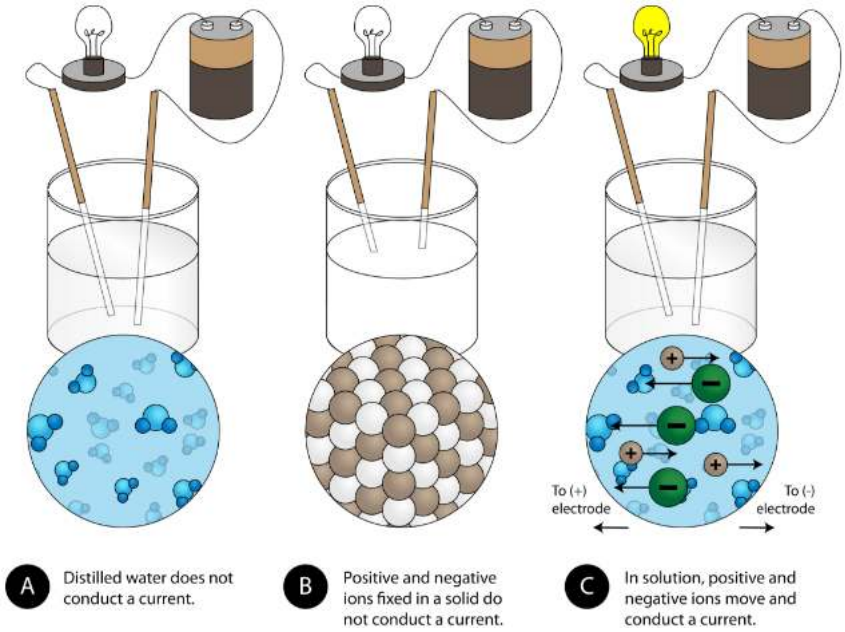


Figure 3.10.3: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

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 3.10.1

Write the dissociation equation of solid NaCl in water.

Solution

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

? Exercise 3.10.1

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.

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3.11: H^+ and OH^- Ions - An Introduction to Acids and Bases

Learning Objectives

- To identify H^+ as an acid and OH^- as a base.

You may have some idea, from your day-to-day experiences, of some chemical substances that are considered acids or bases. Generally, a compound that is sour is recognized as being an acid. Some familiar acids may include citric acid, which is a molecule found in citrus fruits such as lemons and limes, and acetic acid, the molecule that makes up vinegar. Bases, on the other hand, include chemicals such as sodium bicarbonate (baking soda), which is bitter-tasting, and sodium hydroxide, which is found in cleaning substances and is not recommended for ingestion.

More details about acids, bases, and the reactions they undergo will be discussed later in this text. However, because you have just learned about ions and ionic compounds, it is worth pointing out two important ions that are used to identify and distinguish if a substance is acidic or basic; hydrogen ions, H^+, and hydroxide ions, OH^-. In fact, one definition of acids and bases states that an **acid** will produce H^+ when dissolved in water and a **base** will produce a OH^- when dissolved in water.

Ionic compounds that are basic are easily recognized because the hydroxide ion is part of the formula and name. Some common examples are sodium *hydroxide*, $NaOH$, and calcium *hydroxide*, $Ca(OH)_2$. When dissolved in water, sodium hydroxide will split into its constituent ions, sodium ions (Na^+) and hydroxide ions (OH^-) in a 1:1 ratio. However, according to it's chemical formula, calcium hydroxide will produce two hydroxide ions for every one calcium ion, a 1:2 ratio.

Compounds that produce hydrogen ions in water contain one or more hydrogen ions in the chemical formula and usually have special names to help recognize them as acids. Hydrochloric acid (HCl), nitric acid (HNO_3), and carbonic acid (H_2CO_3) are all acids. HCl and HNO_3 each dissolve in water producing a H^+ and an anion (chloride and nitrate respectively). As indicated by the formula for carbonic acid there are two H^+ for every one carbonate ion. The below table lists some common acids. See if you can determine the ratio of H^+ to anions produced when these compounds are dissolved in water.

Table 3.11.1 Common Acids and Their Anions

Acid Name	Acid Formula	Anion Name	Anion Formula
acetic acid	CH_3COOH	acetate ion	CH_3COO^-
carbonic acid	H_2CO_3	bicarbonate ion	HCO_3^-
		carbonate ion	CO_3^{2-}
hydrobromic acid	HBr	bromide ion	Br^-
nitric acid	HNO_3	nitrate ion	NO_3^-
nitrous acid	HNO_2	nitrous ion	NO_2^-
phosphoric acid	H_3PO_4	dihydrogen phosphate ion	$H_2PO_4^-$
		hydrogen phosphate ion	HPO_4^{2-}
		phosphate ion	PO_4^{3-}
sulfuric acid	H_2SO_4	hydrogen sulfate ion	HSO_4^-
		sulfate ion	SO_4^{2-}
sulfurous acid	H_2SO_3	hydrogen sulfite ion	HSO_3^-
		sulfite ion	SO_3^{2-}

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CHAPTER OVERVIEW

4: Molecular Compounds

4.1: Covalent Bonds
4.2: Covalent Bonds and the Periodic Table
4.3: Multiple Covalent Bonds
4.4: Coordinate Covalent Bonds
4.5: Characteristics of Molecular Compounds
4.6: Molecular Formulas and Lewis Structures
4.7: Drawing Lewis Structures
4.8: The Shapes of Molecules
4.9: Polar Covalent Bonds and Electronegativity
4.10: Polar Molecules
4.11: Naming Binary Molecular Compounds

Thumbnail: Covalently bonded hydrogen and carbon in a w:molecule of methane. (CC BY-SA 2.5; DynaBlast via Wikipedia)

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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 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-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.

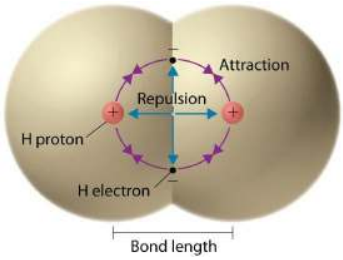


Figure 4.1.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

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.

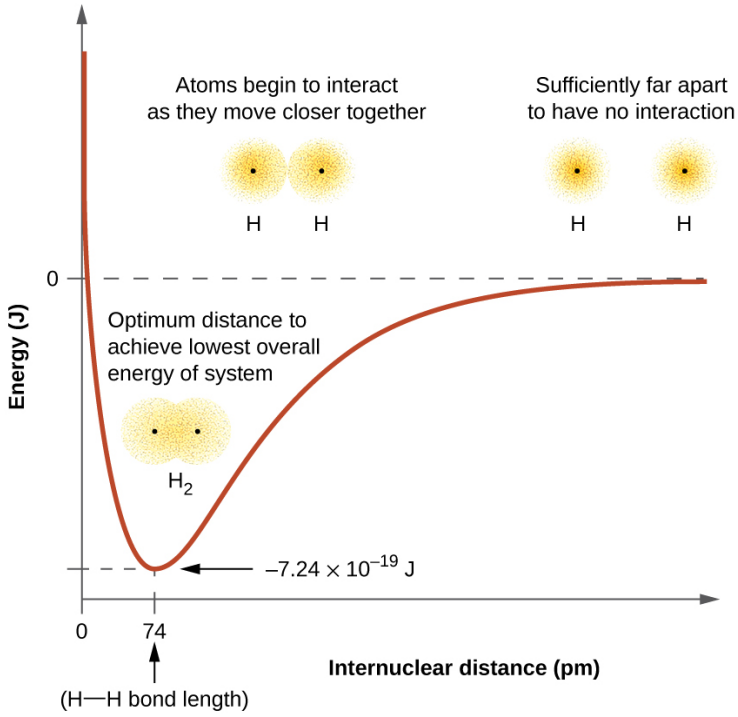


Figure 4.1.2: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

Lewis Structures

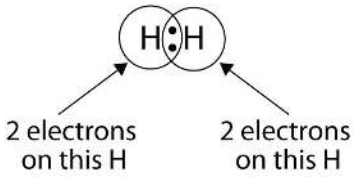
Chemists frequently use Lewis structures to represent covalent bonding in molecular substances. For example, the Lewis symbols of two separate hydrogen atoms are as follows:

$$H\bullet \qquad\qquad \bullet H$$

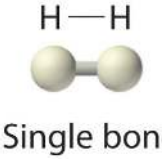
The Lewis structures of two hydrogen atoms sharing electrons looks like this:

$$H{:}H$$

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

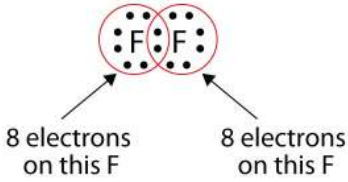
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



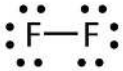
These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.



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 (H_2) and fluorine (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 (H_2)	Oxygen (O_2)	Nitrogen (N_2)	Fluorine (F_2)
Chlorine (Cl_2)	Bromine (Br_2)	Iodine (I_2)	

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4.2: Covalent Bonds and the Periodic Table

Learning Objectives

- Predict the number of covalent bonds formed based on the elements involved and their position on the periodic table.
- Describe the important exceptions to the octet rule.

Diatomic molecules such as hydrogen (H_2), chlorine (Cl_2), fluorine (F_2), etc. containing covalent bonds between two of the same type of atom are only a few examples of the vast number of molecules that can form. Two different atoms can also share electrons and form covalent bonds. For example, water, (H_2O), has two covalent bonds between a single oxygen atom and two hydrogen atoms. Ammonia, (NH_3, is a central nitrogen atom bonded to three hydrogen atoms. Methane, (CH_4, is a single carbon atom covalently bonded to four hydrogen atoms. In these examples the central atoms form different numbers of bonds to hydrogen atoms in order to complete their valence subshell and form octets.

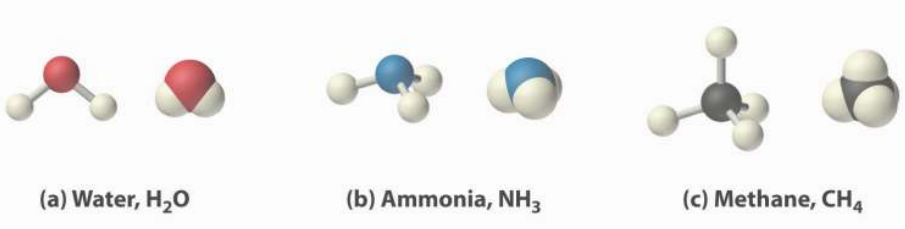
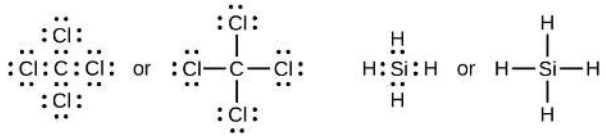


Figure 4.2.4: 3D molecule examples. From left to right: water molecule, ammonia molecule, and methane molecule

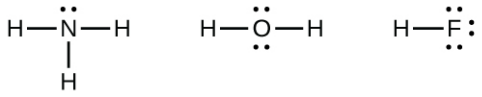
How Many Covalent Bonds Are Formed?

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.



carbon tetrachloride silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

The number of electrons required to obtain an octet determines the number of covalent bonds an atom can form. This is summarized in the table below. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

Table showing 4 different atoms, each of their number of bonds, and each of their number of lone pairs.

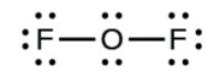
Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14)	4	0

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Nitrogen (Group 15)	3	1
Oxygen (Group 16)	2	2
Fluorine (Group 17)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the *duet rule*. Hydrogen only needs to form one bond to complete a duet of electrons. This is the reason why H is always a terminal atom and never a central atom.

Example 4.2.1

Examine the Lewis structure of OF_2 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?

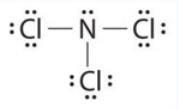


Solution

Yes. F (group 7A) forms one bond and O (group 6A) forms 2 bonds. Each atom is surrounded by 8 electrons. This structure satisfies the octet rule.

Exercise 4.2.1

Examine the Lewis structure of NCl_3 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



Answer

Both Cl and N form the expected number of bonds. Cl (group 7A) has one bond and 3 lone pairs. The central atom N (group 5A) has 3 bonds and one lone pair. Yes, the Lewis structure of NCl_3 follows the octet rule.

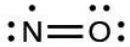
Octet Rule Exceptions

As important and useful as the octet rule is in chemical bonding, there are many covalent molecules with central atoms that do not have eight electrons in their Lewis structures. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient (diminished octet) molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Expanded octet (hypervalent) molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron molecules

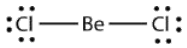
Although they are few, some stable compounds, often called *free radicals*, have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable, odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO, a compound produced in internal combustion engines when oxygen and nitrogen react at high temperatures, is as follows:



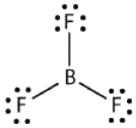
As you can see, the nitrogen and oxygen share four electrons between them. The oxygen atom has an octet of electrons but the nitrogen atom has only seven valence electrons, two electrons in the double bond, one lone pair, and one additional lone electron. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

Electron-deficient molecules

These stable compounds have less than eight electrons around an atom in the molecule, i.e. they have less than an octet. 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:

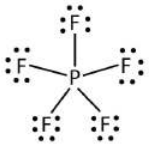


Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:

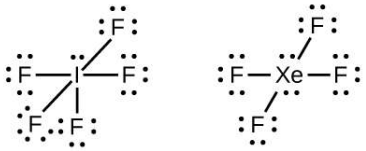


Expanded Octet Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements have expanded octets and are sometimes called hypervalent molecules. Phosphorous pentachloride shares five pairs of electrons for a total of ten electrons in the valence shell.



In some expanded octet molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



Example 4.2.2

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

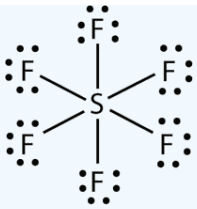
a. ClO
b. SF_6

Solution

1. 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:



2. 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 4.2.2: 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.



Concept Review Exercises

1. How is a covalent bond formed between two atoms?
2. How does covalent bonding allow atoms in group 6A to satisfy the octet rule?

Answers

1. Covalent bonds are formed by two atoms sharing electrons.
2. The atoms in group 6A make two covalent bonds.

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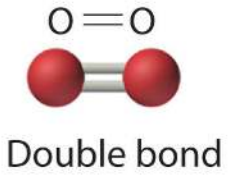
4.3: Multiple Covalent Bonds

Learning Objectives

- Identify when a multiple bond (double or triple) is needed to complete an octet.

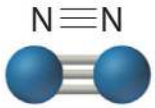
The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***



Double bond

- Three electron pairs shared a ***triple bond***



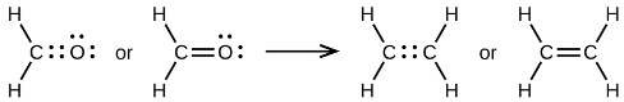
Triple bond

Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms.



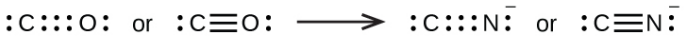
In addition to nitrogen and oxygen, carbon will also commonly form multiple bonds to complete valence octets. Additional examples involving these three atoms are shown below.

A double bond is formed between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

A triple bond is formed between carbon and oxygen in carbon monoxide (CO) and between carbon and nitrogen in the cyanide ion (CN^-):



carbon monoxide cyanide ion

Example 4.3.1: Writing Lewis Structures

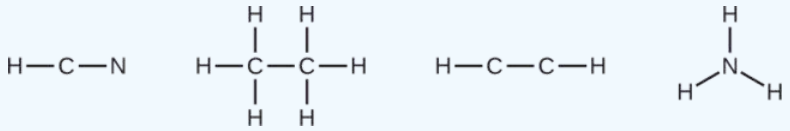
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

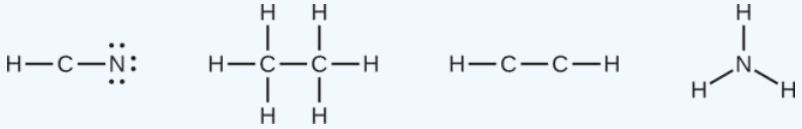
Calculate the number of valence electrons.

- HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
- H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
- HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
- NH_3: (5 × 1) + (3 × 1) = 8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

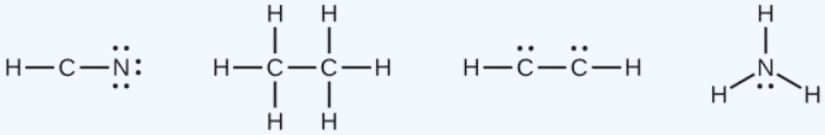


Where needed, distribute electrons to the terminal atoms:



- HCN: six electrons placed on N
- H_3CCH_3: no electrons remain
- HCCH: no terminal atoms capable of accepting electrons
- NH_3: no terminal atoms capable of accepting electrons

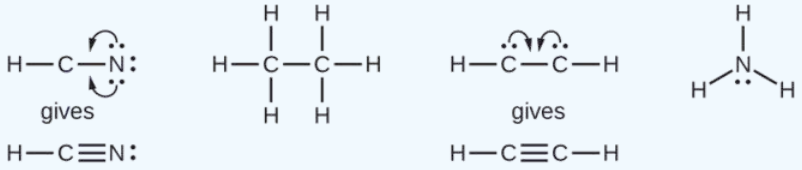
Where needed, place remaining electrons on the central atom:



- HCN: no electrons remain
- H_3CCH_3: no electrons remain
- HCCH: four electrons placed on carbon
- NH_3: two electrons placed on nitrogen

Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

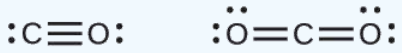
- HCN: form two more C–N bonds
- H_3CCH_3: all atoms have the correct number of electrons
- HCCH: form a triple bond between the two carbon atoms
- NH_3: all atoms have the correct number of electrons



? Exercise 4.3.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



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4.4: Coordinate Covalent Bonds

Learning Objectives

- Describe the difference between a covalent bond and a coordinate covalent bond.
- Identify molecules that form coordinate covalent bonds.

Remember when you were younger, and were told to share your favorite toy with your brother, sister, or friend? You probably didn't want to share, but did anyway. It likely turned out that you had more fun playing with the toy together than if you had kept it to yourself. Atoms often share electrons with other atoms that have nothing to contribute to the situation forming a **coordinate covalent bond**; the end result is a new structure.

Coordinate Covalent Bonds

Each of the covalent bonds that we have looked at so far has involved each of the atoms that are bonding contributing one of the electrons to the shared pair. There is an alternate type of covalent bond in which one of the atoms provides *both* of the electrons in a shared pair. Carbon monoxide, CO, is a toxic gas that is released as a byproduct during the burning of fossil fuels. The bonding between the C atom and the O atom can be thought of in the following procession:

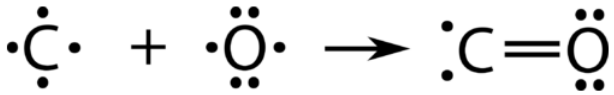


Figure 4.4.2: Formation of a CO double bond (incorrect structure). (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

At this point, a double bond has formed between the two atoms, with each atom providing one of the electrons to each bond. The oxygen atom now has a stable octet of electrons, but the carbon atom only has six electrons and is unstable. This situation is resolved if the oxygen atom contributes one of its lone pairs in order to make a third bond with the carbon atom.

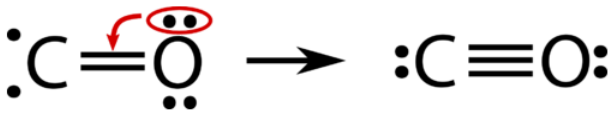
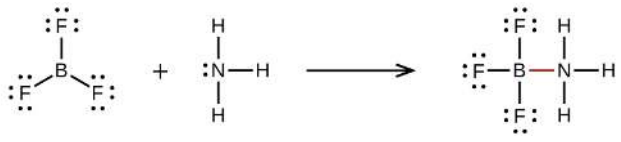


Figure 4.4.3: Correct CO structure. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The carbon monoxide molecule is correctly represented by a triple covalent bond between the carbon and oxygen atoms. One of the bonds formed is a coordinate covalent bond, a covalent bond in which one of the atoms contributes both of the electrons in the shared pair. Once formed, a coordinate covalent bond is the same as any other covalent bond. It is not as if the two conventional bonds in the CO molecule are stronger or different in any other way than the coordinate covalent bond.

Electron-deficient molecules, like $\mathrm{BF_3}$, are very reactive and will often combine with other molecules forming coordinate covalent bonds. The central boron atom in $\mathrm{BF_3}$ does not have eight electrons, and is therefore very reactive. It can readily combine with a molecule containing a central atom with a lone pair of electrons. For example, $\mathrm{NH_3}$ reacts with $\mathrm{BF_3}$ because the lone pair on nitrogen can be shared with the boron atom:



Summary

- Coordinate covalent bonds can form when one atom provides a lone pair of electrons to the bond.
- Coordinate covalent bonds are as strong as other covalent bonds.

Review

1. Where does the third covalent bond in the CO molecule come from?
2. Why is the incorrect structure for CO above wrong?

3. Are coordinate covalent bonds stronger or weaker than regular covalent bonds?

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4.5: Characteristics of Molecular Compounds

Learning Objectives

- Compare the properties of ionic and molecular compounds.

The physical state and properties of a particular compound depend in large part on the type of chemical bonding it displays. Molecular compounds, sometimes called covalent compounds, display a wide range of physical properties due to the different types of intermolecular attractions such as different kinds of polar interactions. The melting and boiling points of molecular compounds are generally quite low compared to those of ionic compounds. This is because the energy required to disrupt the *intermolecular forces* (discussed further in a later chapter) between molecules is far less than the energy required to break the ionic bonds in a crystalline ionic compound. Since molecular compounds are composed of neutral molecules, their electrical conductivity is generally quite poor, whether in the solid or liquid state. Ionic compounds do not conduct electricity in the solid state because of their rigid structure, but conduct well when either molten or dissolved into a solution. The water solubility of molecular compounds is variable and depends primarily on the type of intermolecular forces involved. Substances that exhibit hydrogen bonding or dipole-dipole forces are generally water soluble, whereas those that exhibit only London dispersion forces are generally insoluble. Most, but not all, ionic compounds are quite soluble in water. The table below summarizes some of the differences between ionic and molecular compounds.

Table 4.5.1: Comparison of Ionic and Molecular Compounds

Property	Ionic Compounds	Molecular Compounds
Type of elements	Metal and nonmetal	Nonmetals only
Bonding	Ionic - transfer of electron(s) between atoms	Covalent - sharing of pair(s) of electrons between atoms
Representative unit	Formula unit	Molecule
Physical state at room temperature	Solid	Gas, liquid, or solid
Water solubility	Usually high	Variable
Melting and boiling temperatures	Generally high	Generally low
Electrical conductivity	Good when molten or in solution	Poor

In summary, covalent compounds are softer, have lower boiling and melting points, are more flammable, are less soluble in water and do not conduct electricity compared to ionic compounds. The individual melting and boiling points, solubility and other physical properties of molecular compounds depend on molecular polarity.

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4.6: Molecular Formulas and Lewis Structures

Learning Objectives

- Understand the different ways to represent molecules.

There are many "universal languages" in the world. Musicians of every culture recognize music embodied in a series of notes on a staff. This passage from a Bach cello suite could be played by any trained musician from any country, because there is an agreement as to what the symbols on the page mean. In the same way, molecules are represented using symbols and a language that all chemists agree upon.
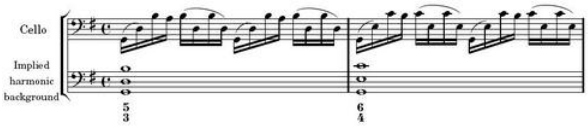


Figure 4.6.1 (Credit: J. S. Bach; Source: http://commons.wikimedia.org/wiki/File:Bach_cello_harmony.JPG(opens in new window); License: Public Domain)

Molecular Formulas

A **molecular formula** is a chemical formula of a molecular compound that shows the kinds and numbers of atoms present in a molecule of the compound. Ammonia is a compound of nitrogen and hydrogen as shown below:

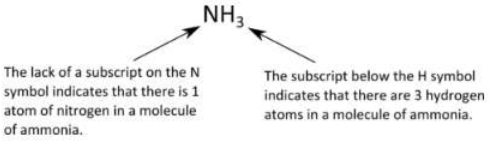


Figure 4.6.2: The molecular formula for ammonia. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Note from the example that there are some standard rules to follow in writing molecular formulas. The number of atoms of each kind is indicated by a subscript following the atom. If there is only one atom, no number is written. If there is more than one atom of a specific kind, the number is written as a subscript following the atom. We would not write N_3H for ammonia, because that would mean that there are three nitrogen atoms and one hydrogen atom in the molecule, which is incorrect.

Although it is useful for describing a molecule, the molecular formula does not tell us anything about the shape of the molecule, where the different atoms are, or what kinds of bonds are formed. **Structural formulas** are much more useful to communicate more detailed information about a molecule because they show which atoms are bonded to one another and, in some cases, the approximate arrangement of the atoms in space. Knowing the structural formula of a compound enables chemists to create a three-dimensional model, which provides information about how that compound will behave physically and chemically.

Figure $4.6.3$ shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (Figure $4.6.3a$) gives only the number of each kind of atom; writing methanol as CH_4O tells nothing about its structure. In contrast, the structural formula (Figure $4.6.3b$) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure $4.6.3$) and the perspective drawing (Figure $4.6.3d$) show the three-dimensional structure of the molecule. The latter (also called a wedge-and-dash representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure $4.6.3$) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. In addition, in a space-filling model, atoms at the “front” of the molecule may obscure atoms at the “back.”

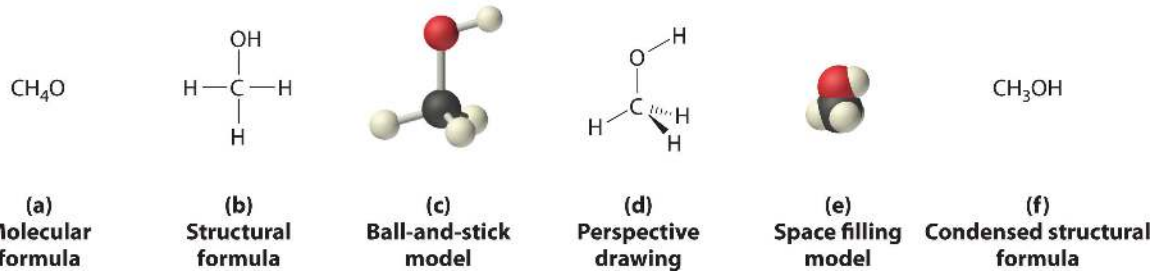


Figure 4.6.3: Different Ways of Representing the Structure of a Molecule. (a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a condensed structural formula (part (f) in Figure 4.6.3), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is CH_3OH, which indicates that the molecule contains a CH_3 unit that looks like a fragment of methane (CH_4). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

Example 4.6.1: Molecular Formulas

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

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

Given: condensed structural formula

Asked for: molecular formula

Strategy:

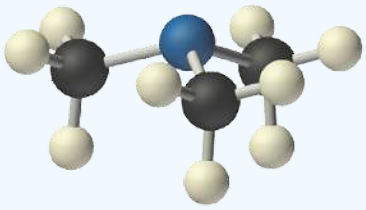
A. Identify every element in the condensed structural formula and then determine whether the compound is organic or inorganic.
B. As appropriate, use either organic or inorganic convention to list the elements. Then add appropriate subscripts to indicate the number of atoms of each element present in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

Solution:

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

a. **A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula S_2Cl_2.
b. **A** Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and hydrogen atoms, so it is organic. **B** As with all organic compounds, C and H are written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $C_2H_6O_2$.

c. **A** The condensed structural formula shows that trimethylamine contains three CH_3 units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. **B** According to the convention for organic compounds, C and H are written first, giving the molecular formula C_3H_9N.

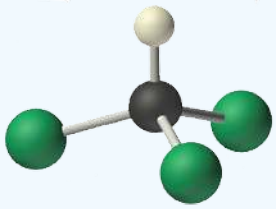


Trimethylamine

Exercise 4.6.1: Molecular Formulas

Write the molecular formula for each molecule.

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



Chloroform

Answer a

$CHCl_3$

Answer b

N_2H_4

Answer c

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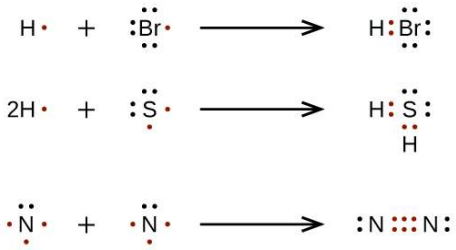
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4.7: Drawing Lewis Structures

Learning Objectives

- Draw Lewis structures for molecules.

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules, it is helpful to follow the step-by-step procedure outlined here:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

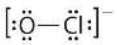
1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



Because this structure gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for a molecular ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

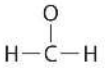
The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



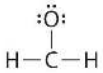
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

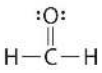
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

Example 4.7.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

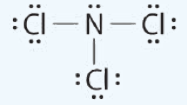
Asked for: Lewis electron structures

Strategy:

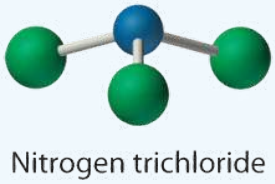
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

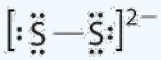


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

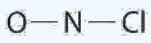


Nitrogen trichloride

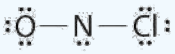
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



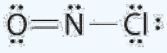
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



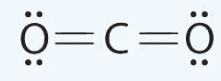
Nitrosyl chloride

? Exercise 4.7.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer

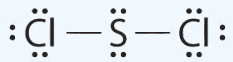
1.



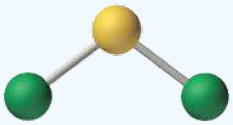


Carbon dioxide

2.



Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.



Sulfur dichloride

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4.8: The Shapes of Molecules

Learning Objectives

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced “vesper”), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

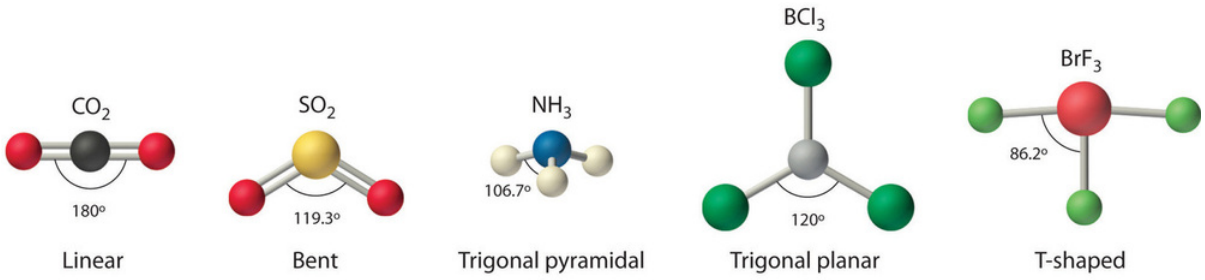


Figure 4.8.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form **electron groups** (regions of electron density), which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 4.8.1.

It is important to note that electron group geometry around a central atom is *not* the same thing as its molecular structure. Electron group geometries describe ***all*** regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms* alone, not including the lone pair electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron group geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure** (or molecular shape). The electron group geometries will be the *same* as the molecular structures when there are no lone electron pairs around the central atom, but they will be *different* when there are lone pairs present on the central atom.

Predicting Electron Group Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine electron group geometry and molecular structures (molecular shape):

1. Draw the Lewis structure of the molecule or polyatomic ion.

2. Count the number of electron groups or regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one electron group.
3. Determine the electron group geometry by placing the groups as far apart as possible.
4. Determine the molecular structure (looking at the bonded groups only).

Table 4.8.1 summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table 4.8.1: Summary of Electron Group Geometries and Molecular Structures

Number of Electron Groups on Central Atom	Number of Bonding Groups	Number of Lone Pairs	Electron Group Geometry	Molecular Structure
2	2	0	linear	linear
3	3	0	trigonal planar	trigonal planar
3	2	1	trigonal planar	bent 120°
4	4	0	tetrahedral	tetrahedral
4	3	1	tetrahedral	trigonal pyramidal
4	2	2	tetrahedral	bent 109°

Two Electron Groups

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, which is 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 structure is linear. Examples include BeH_2 and CO_2:



Figure 4.8.2: Beryllium hydride and carbon dioxide bonding.

Three Electron Groups

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:

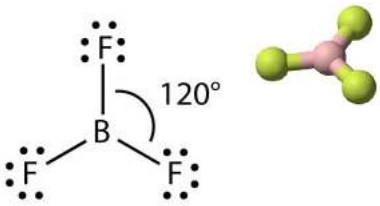


Figure 4.8.3: Boron trifluoride bonding. (CK12 Licence)

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:

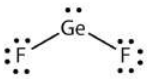


Figure 4.8.4: Germanium difluoride bonding.

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 molecular structure is called **bent 120°** or angular.

Four Electron Groups

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron with bond angles of approximately 109.5°. If there are four atoms attached to these electron groups, then the molecular structure is also **tetrahedral**. Methane (CH_4) is an example.



Figure 4.8.5: 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.

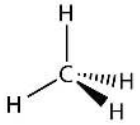


Figure 4.8.6: Methane bonding. (CK12 Licence)

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.

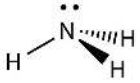


Figure 4.8.7: Ammonia bonding. (CK12 Licence)

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 4.8.8: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is **bent 109°** 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.

Shapes of Molecules with Double or Triple Bonds

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure 4.8.9.



Figure 4.8.9: 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*.

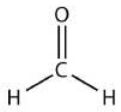


Figure 4.8.10: Formaldehyde bonding.

(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.

Example 4.8.1

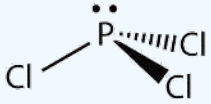
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

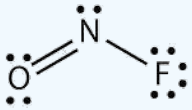
The first step is to draw the Lewis structure of the molecule.

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 4.8.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

Exercise 4.8.2

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.)

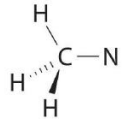
Answer

Trigonal planar about both central C atoms.

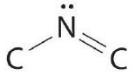
Molecules With Multiple Central Atoms

The VSEPR model can be used to predict the structure of somewhat more complex molecules with more than one central atom by using VSEPR as described above for each central atom individually. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin.

Start by looking at the electron groups around the first carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. There are four groups or electrons or four bonds around the carbon. We can therefore predict the CH_3–N portion of the molecule to be roughly *tetrahedral*, similar to methane:



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



One carbon bonded to nitrogen and another carbon double bonded to the nitrogen. The nitrogen has one lone pair.

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron groups. Thus according to the VSEPR model, the C–N=C fragment should be *bent* with an angle ~120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:

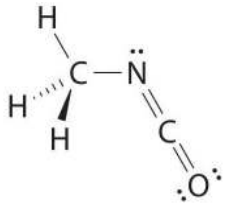


Figure 4.8.11). The Lewis Structure of Methyl Isocyanate

Three hydrogens are bonded to a carbon. The carbon is also bonded to a nitrogen. The nitrogen is double bonded to another carbon. The second carbon is double bonded to an oxygen. The nitrogen has one lone pair. The oxygen has two lone pairs.

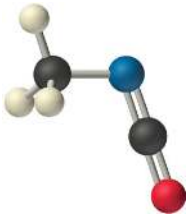


Figure 4.8.12: The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

Example 4.8.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C{\equiv}CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 4.8.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond

in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

? Exercise 4.8.3

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

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4.9: Polar Covalent Bonds and Electronegativity

Learning Objectives

- Describe electronegativity and polarity.
- Use electronegativity values to predict bond polarity.

Our discussions of bonding thus far have focused on two types, ionic and covalent. In ionic bonds, like $NaCl$, electrons are *transferred*; the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom, and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions. In covalent bonding, unpaired electrons from individual atoms are *shared* in order to fill the valence shell of each atom. When a covalent bond is formed between the same type of atoms, such as Cl_2, the electrons are *shared equally* between the two. However, when a covalent bond is formed between different types of atoms, the electrons are not necessarily shared equally. In these compounds their bond character falls *between* the two extremes: transferred and shared equally.

Bond Polarity

As demonstrated below, **bond polarity** is a useful concept for describing the sharing of electrons between atoms, within a covalent bond:

- A **nonpolar covalent bond** (Figure $4.9.1a$)is one in which the electrons are shared *equally* between two atoms.
- A **polar covalent bond** (Figure $4.9.1b$) is one in which one atom has a greater attraction for the electrons than the other atom.
- If the relative attraction of an atom for electrons is great enough, then the bond is an **ionic bond (**Figure $4.9.1c$).

Electron density in a polar bond is distributed unevenly and is greater around the atom that attracts the electrons more than the other. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Note that the shaded area around Cl in Figure $4.9.1b$ is much larger than it is around H. This imbalance in electron density results in a buildup of *partial negative charge* (designated as δ−) on one side of the bond (Cl) and a *partial positive charge* (designated δ+) on the other side of the bond (H).

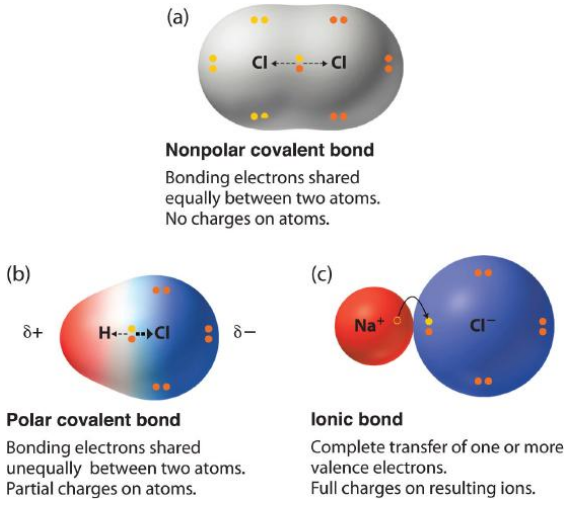


Figure 4.9.1: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred rather than shared. To judge the relative polarity of a covalent bond, chemists use electronegativity, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

Electronegativity

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity**, defined as the *relative ability* of an atom to attract electrons to itself in a chemical compound. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom's electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.*

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

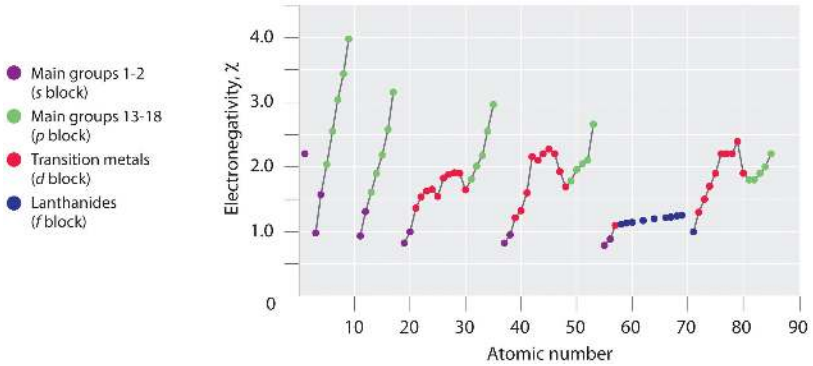


Figure 4.9.2: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations (trends) in Pauling's electronegativity values are illustrated in Figures 4.9.2 and 4.9.3. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine is the most electronegative element and cesium is the least electronegative nonradioactive element. Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl, and N, S, and Br).

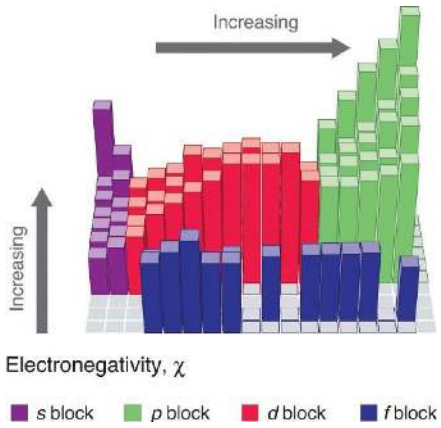


Figure 4.9.3: Pauling Electronegativity Values of the *s*-, *p*-, *d*-, and *f*-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960).

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

The polarity of a covalent bond can be judged by determining the difference in the electronegativities of the two atoms making the bond. The greater the difference in electronegativities, the greater the imbalance of electron sharing in the bond. Although there are no hard and fast rules, the general rule, (see Figure 4.9.5), is if the difference in electronegativities is less than about 0.4, the bond is considered nonpolar; if the difference is greater than 0.4, the bond is considered polar. If the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond.

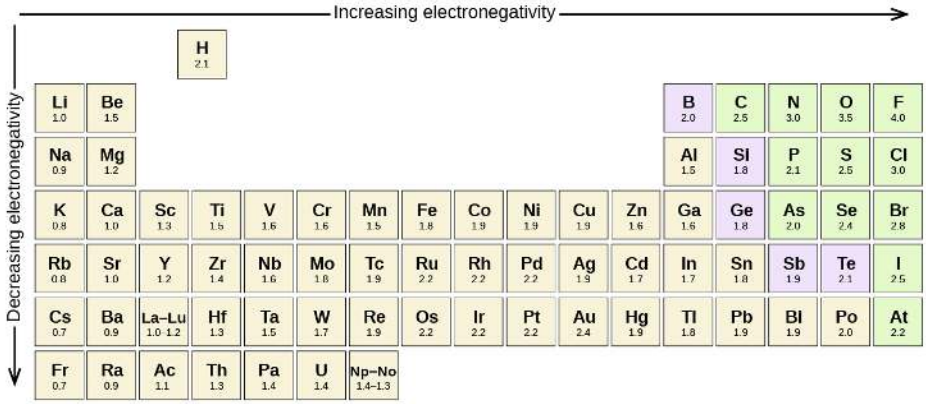
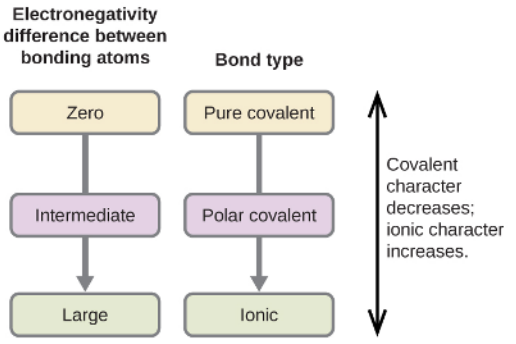


Figure 4.9.4 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 4.9.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

Example 4.9.1

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

a. C and H
b. H and H
c. Na and Cl
d. O and H

Solution

a. Carbon has an electronegativity of 2.5, while the value for hydrogen is 2.1. The difference is 0.4, which is rather small. The C–H bond is therefore considered nonpolar.
b. Both hydrogen atoms have the same electronegativity value—2.1. The difference is zero, so the bond is nonpolar.
c. Sodium's electronegativity is 0.9, while chlorine's is 3.0. The difference is 2.1, which is rather high, and so sodium and chlorine form an ionic compound.
d. With 2.1 for hydrogen and 3.5 for oxygen, the electronegativity difference is 1.4. We would expect a very polar bond. The sharing of electrons between O and H is unequal with the electrons more strongly drawn towards O.

Exercise 4.9.1

Describe the electronegativity (EN) difference between each pair of atoms and the resulting polarity (or bond type).

a. C and O
b. K and Br
c. N and N
d. Cs and F

Answer a:

The EN difference is 1.0 , hence polar. The sharing of electrons between C and O is unequal with the electrons more strongly drawn towards O.

Answer b:

The EN difference is greater than 1.8, hence ionic.

Answer c:

Identical atoms have zero EN difference, hence nonpolar.

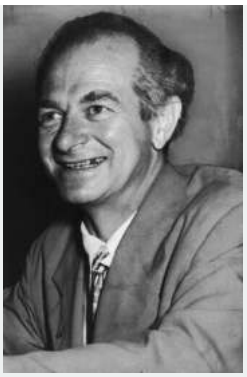
Answer d:

The EN difference is greater than 1.8, hence ionic.

Looking Closer: Linus Pauling

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–94) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.



Linus Pauling was one of the most influential chemists of the 20th century.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal.

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4.10: Polar Molecules

Learning Objectives

- Recognize bond characteristics of covalent compounds: bond length and bond polarity.
- Use electronegativity values to predict bond polarity.

If there is only one bond in the molecule, the bond polarity determines the *molecular polarity*. Any diatomic molecule in which the two atoms are the same element must be a nonpolar molecule. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule where one end of the molecule is slightly positive, while the other end is slightly negative. 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. Hence, a molecule with two poles has a **dipole moment**.

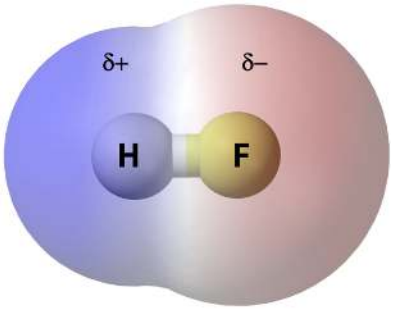


Figure 4.10.1: A molecular dipole results from the unequal distribution of electron density throughout a molecule. The H, with less electron density is partially positive and the F, with more electron density is partially negative. (Figure modified from: Wikipedia [en.Wikipedia.org])

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 with carbon in the center and two oxygens at the terminal ends. 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 pointing in opposite directions, they *cancel out* and the overall molecular polarity of CO_2 is zero (no net dipole), therefore CO_2 is a *nonpolar molecule*.

Water has a bent molecular structure because it has four electron groups, two bonded groups and two lone electron groups on the central oxygen atom. The individual O–H bond dipoles point from the slightly positive H atoms toward the more electronegative O atom. Because of the bent shape, the dipoles, which are equal in strength, both point towards the oxygen atom and will not cancel each other out, therefore, the water molecule is polar. In the figure below, you can see that the oxygen end of the molecule is slightly negative and the hydrogen side is slightly positive, there is a separation of charge throughout the whole molecule, a **net dipole** (shown in blue) that points upward.

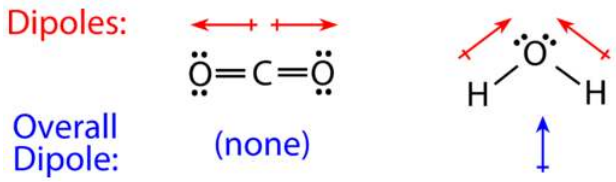


Figure 4.10.2: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. In contrast, water is polar because the OH bond dipole moments do not cancel out. There is a net separation of charge or overall dipole moment.

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.

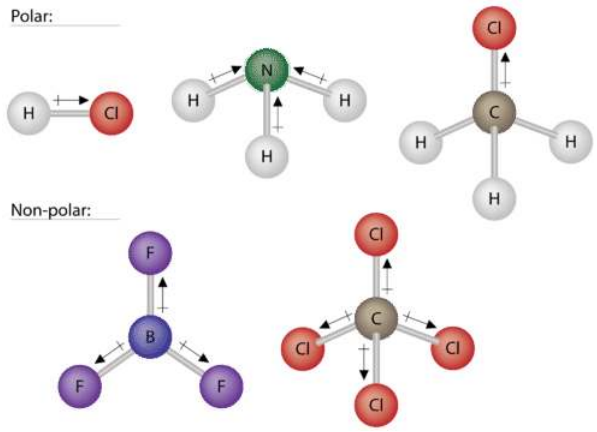


Figure 4.10.3: Some examples of polar and nonpolar molecules based on molecular geometry.

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 4.10.4). 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.

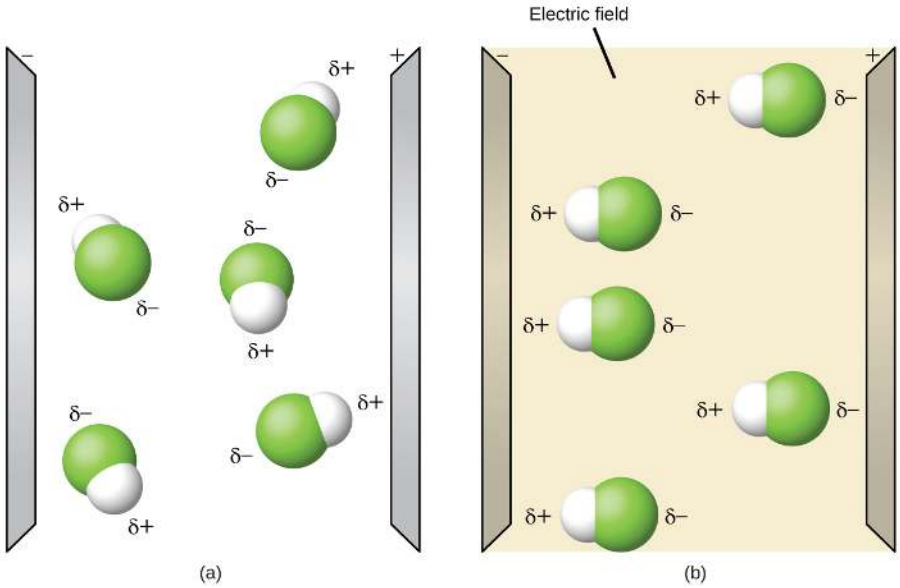


Figure 4.10.4: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

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 4.10.1: Polarity Simulations

Open the molecule polarity simulation (above) and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 4.10.1

Determine the partial charges that will give the largest possible bond dipoles.

Answer

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

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4.11: Naming Binary Molecular Compounds

Learning Objectives

- Name binary molecular compounds.

Naming *binary* (two-element) covalent compounds is very 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*. Unlike for ionic compounds, molecular compounds can be formed using the same elements in different ratios. Therefore, it is important to indicate the number of each type of atom, using a system of numerical prefixes, listed in Table 4.11.1. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table 4.11.1: 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.

Let us practice by naming the compound whose molecular formula is CCl_4. The name begins with the name of the first element carbon. The second element, chlor*ine*, becomes chlor*ide*, and we attach the correct numerical prefix ("tetra-") to indicate that the molecule contains four chlorine atoms. Putting these pieces together gives the name *carbon tetrachloride* for this compound.

Example 4.11.1

Write the molecular formula for each compound.

a. chlorine trifluoride
b. phosphorus pentachloride
c. sulfur dioxide
d. dinitrogen pentoxide

Solution

If there is no numerical prefix on the first element's name, we can assume that there is only one atom of that element in a molecule.

a. ClF_3
b. PCl_5
c. SO_2
d. N_2O_5 (The *di-* prefix on nitrogen indicates that two nitrogen atoms are present.)

Exercise 4.11.1

Write the molecular formula for each compound.

a. nitrogen dioxide
b. dioxygen difluoride
c. sulfur hexafluoride
d. selenium monoxide

Answer a:

a. NO_2

Answer b:

O_2F_2

Answer c:

SF_6

Answer d:

SeO

Because it is so unreactive, sulfur hexafluoride is used as a spark suppressant in electrical devices such as transformers.

Example 4.11.2

Write the name for each compound.

a. BrF_5
b. S_2F_2
c. CO

Solution

a. bromine pentafluoride
b. disulfur difluoride
c. carbon monoxide

Exercise 4.11.2

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

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

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system that we will introduce later.

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CHAPTER OVERVIEW

5: Classification and Balancing of Chemical Reactions

5.1: Chemical Equations
5.2: Balancing Chemical Equations
5.3: Precipitation Reactions and Solubility Guidelines
5.4: Acids, Bases, and Neutralization Reactions
5.5: Redox Reactions
5.6: Recognizing Redox Reactions
5.7: Net Ionic Equations

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5.1: Chemical Equations

Learning Objectives

- Define *chemical reaction*.
- Understand the Law of Conservation of Matter

Water (H_2O) is composed of hydrogen and oxygen. Suppose we imagine a process in which we take some elemental hydrogen (H_2) and elemental oxygen (O_2) and let them react to make water. The statement

"hydrogen and oxygen react to make water"

is one way to represent that process, which is called a chemical reaction. Figure 5.1.1 shows a rather dramatic example of this very reaction.

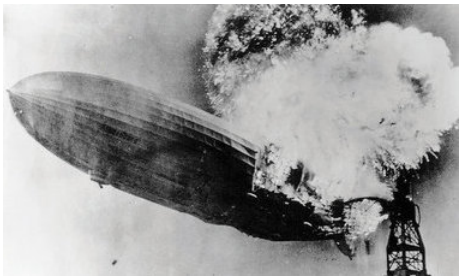


Figure 5.1.1: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin *SS Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

To simplify the writing of reactions, we use formulas instead of names when we describe a reaction. We can also use symbols to represent other words in the reaction. A plus sign connects the initial substances (and final substances, if there is more than one), and an arrow ($\rightarrow$) represents the chemical change:

$$\mathrm{H_2 + O_2 \rightarrow H_2O} \tag{5.1.1}$$

This statement is one example of a **chemical equation**, an abbreviated way of using symbols to represent a chemical change. The substances on the left side of the arrow are called **reactants**, and the substances on the right side of the arrow are called **products**. It is not uncommon to include a phase label with each formula—(s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for a substance dissolved in water, also known as an *aqueous solution*. If we included phase labels for the reactants and products, under normal environmental conditions, the reaction would be as follows:

$$\mathrm{H_2(g) + O_2(g) \rightarrow H_2O(\ell)} \tag{5.1.2}$$

This equation is still not complete because *it does not satisfy the* ***law of conservation of matter***. Count the number of atoms of each element on each side of the arrow. On the reactant side, there are two H atoms and two O atoms; on the product side, there are two H atoms and only one oxygen atom. The equation is not balanced because the number of oxygen atoms on each side is not the same (Figure 5.1.2).

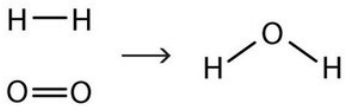


Figure 5.1.2: Balanced—Yes or No? By counting the atoms of each element, we can see that the reaction is not balanced as written.

To make this chemical equation conform to the law of conservation of matter, we must revise the amounts of the reactants and the products as necessary to get the *same* number of atoms of a given element on each side. Because every substance has a characteristic chemical formula, we cannot change the chemical formulas of the individual substances. For example, we cannot change the formula for elemental oxygen to O. However, we can assume that different numbers of reactant molecules or product molecules may be involved. For instance, perhaps two water molecules are produced, not just one:

$$\mathrm{H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)} \tag{5.1.3}$$

The **2** preceding the formula for water is called a **coefficient**. It implies that two water molecules are formed. There are now two oxygen atoms on each side of the equation.

> This point is so important that we should repeat it. You *cannot* change the formula of a chemical substance to balance a chemical reaction! You *must* use the proper chemical formula of the substance.

Unfortunately, by inserting the coefficient 2 in front of the formula for water, we have also changed the number of hydrogen atoms on the product side as well. As a result, we no longer have the same number of hydrogen atoms on each side. This can be easily fixed, however, by putting a coefficient of 2 in front of the diatomic hydrogen reactant:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell) \tag{5.1.4}$$

Now we have four hydrogen atoms and two oxygen atoms on each side of the equation. The law of conservation of matter is satisfied because we now have the *same number* of atoms of each element in the reactants and in the products. We say that the reaction is now **balanced** (Figure 5.1.3). Note: The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

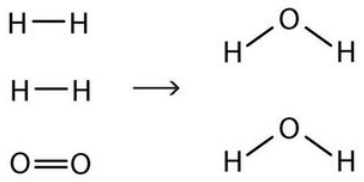


Figure 5.1.3: Balanced—Yes or No? By counting the atoms of each element, we can see that the reaction is now balanced.

Proper chemical equations should be balanced. Writing balanced reactions is a chemist's way of acknowledging the law of conservation of matter.

mple

Is each chemical equation balanced?

a. $2Na(s) + O_2(g) \rightarrow 2Na_2O(s)$
b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$
c. $AgNO_3(aq) + 2KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$

Solution

a. By counting, we find two sodium atoms and two oxygen atoms in the reactants and four sodium atoms and two oxygen atoms in the products. This equation is not balanced.
b. The reactants have one carbon atom, four hydrogen atoms, and four oxygen atoms. The products have one carbon atom, four hydrogen atoms, and four oxygen atoms. This equation is balanced.
c. The reactants have one silver atom, one nitrogen atom, three oxygen atoms, two potassium atoms, and two chlorine atoms. The products have one silver atom, one chlorine atom, one potassium atom, one nitrogen atom, and three oxygen atoms. Because there are different numbers of chlorine and potassium atoms, this equation is not balanced.

rcise

Is each chemical equation balanced?

a. $2Hg_{(\ell)} + O_{2(g)} \rightarrow Hg_2O_{2(s)}$
b. $C_2H_{4(g)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(\ell)}$
c. $Mg(NO_3)_{2(s)} + 2Li_{(s)} \rightarrow Mg_{(s)} + 2LiNO_{3(s)}$.

Answer a:

balanced

Answer b:

O is not balanced; the 4 atoms of oxygen on the left does not balance with the 6 oxygen atoms on the right

Answer c:

balanced

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5.2: Balancing Chemical Equations

Learning Objectives

- Balance chemical equations.

How does one balance a chemical equation, starting with the correct formulas of the reactants and products? Basically, a back-and-forth (or trial-and-error) approach is adopted, counting the number of atoms of one element on one side, checking the number of atoms of that element on the other side, and changing a coefficient if necessary. Then check another element, going back and forth from one side of the equation to another, until each element has the same number of atoms on both sides of the arrow. In many cases, it does not matter which element is balanced first and which is balanced last, as long as all elements have the same number of atoms on each side of the equation.

Below are guidelines for writing and balancing chemical equations.

1. Determine the correct chemical formulas for each reactant and product. Write the skeleton equation.
2. Count the number of atoms of each element that appears as a reactant and as a product. If a polyatomic ion is unchanged on both sides of the equation, count it as a unit.
3. Balance each element one at a time by placing coefficients in front of the formulas. No coefficient is written for a 1. It is best to begin by balancing elements that only appear in one chemical formula on each side of the equation. NEVER change the subscripts in a chemical formula - you can only balance equations by using coefficients.
4. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
5. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

For example, to balance the equation

Step 1: Write the skeleton equation with the correct formulas.

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + HCl} \tag{5.2.1}$$

Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	**Products**
1 C atom	1 C atom
4 H ions	1 H ions
2 Cl atom	5 Cl atoms

(5.2.2)

*Step 3: W*e find that both sides are already balanced with one carbon atom. So we proceed to balance the hydrogen atoms. We find that the reactant side has four hydrogen atoms, so the product side must also have four hydrogen atoms. This is balanced by putting a 4 in front of the HCl:

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{5.2.3}$$

Reactants	**Products**
1 C atom	1 C atom
4 H ions	4 H ions
2 Cl atom	8 Cl atoms

(5.2.4)

Now each side has four hydrogen atoms. The product side has a total of eight chlorine atoms (four from the CCl_4 and four from the four molecules of HCl), so we need eight chlorine atoms as reactants. Because elemental chlorine is a diatomic molecule, we need four chlorine molecules to get a total of eight chlorine atoms. We add another 4 in front of the $\mathrm{Cl_2}$ reactant:

$$\mathrm{CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{5.2.5}$$

Reactants	**Products**
1 C atom	1 C atom
4 H ions	4 H ions
8 Cl atom	8 Cl atoms

(5.2.6)

Step 3: Now we check: each side has one carbon atom, four hydrogen atoms, and eight chlorine atoms. The chemical equation is balanced. And, the coefficients are in the lowest possible ratio.

Example 5.2.2

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

Step 1: Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{5.2.7}$$

Step 2: Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	**Products**
1 Pb atom	1 Pb atom
2 $\mathrm{NO_3^-}$ ions	1 $\mathrm{NO_3^-}$ ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

(5.2.8)

Step 3: Solve. The nitrate ions and the chlorine atoms are unbalanced. Start by placing a 2 in front of the NaCl. This increases the reactant counts to 2 Na atoms and 2 Cl atoms. Then place a 2 in front of the $\mathrm{NaNO_3}$. The result is:

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{NaCl}\,(aq) \rightarrow 2\mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{5.2.9}$$

Step 4: The new count for each atom and polyatomic ion becomes:

Reactants	**Products**
1 Pb atom	1 Pb atom
2 $\mathrm{NO_3^-}$ ions	2 $\mathrm{NO_3^-}$ ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

(5.2.10)

Step 5: Think about the result.

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation. And, the coefficients are in the lowest possible ratio.

Exercise 5.2.2

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose ($C_6H_{12}O_6$) are converted to ethanol (C_2H_5OH) and carbon dioxide CO_2. Write a balanced chemical reaction for the fermentation of glucose.



Commercial use of fermentation. *(a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.*

Answer

$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$

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5.3: Precipitation Reactions and Solubility Guidelines

Learning Objectives

- Use solubility rules to predict whether a precipitate will form.
- Write and balance chemical equations for precipitation reactions.

There are many types of chemical reactions that you will learn about in chemistry. In this chapter, we will focus on some reactions of ionic compounds: *precipitation reactions* (a type of *double-replacement reaction*), *acid-base neutralization reactions*, and *oxidation-reduction reactions*.

The practice of barter (trading one thing for another) has been in existence since the beginning of time. In the past, for example, items like chickens were bartered for newspapers. Person A had something that person B wanted, and vice versa. So, when person A and person B traded items, they each had something new. Some chemical reactions are like that—compounds swap parts, and the products are new materials.

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:

$$\mathrm{AB} + \mathrm{CD} \rightarrow \mathrm{AD} + \mathrm{CB} \tag{5.3.1}$$

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:

$$2\mathrm{KI}\,(aq) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow 2\mathrm{KNO_3}\,(aq) + \mathrm{PbI_2}\,(s) \tag{5.3.2}$$

There are very strong attractive forces that occur between Pb^{2+} and I^{-} ions and the result is a brilliant yellow precipitate (see Figure $5.3.1$ below). The other product of the reaction, potassium nitrate, remains soluble.



Figure $5.3.1$: Formation of lead iodide precipitate. (CC BY-NC; CK-12)

To judge whether double-replacement reactions will occur, we need to know what kinds of ionic compounds form precipitates. For this, we use **solubility rules**, which are general statements that predict which ionic compounds dissolve (are soluble) and which do not (are not soluble, or insoluble). Table $5.3.1$ lists some general solubility rules. We need to consider each ionic compound (both the reactants and the possible products) in light of the solubility rules. If a compound is soluble, we use the (*aq*) label with it, indicating that it dissolves. If a compound is not soluble, we use the (*s*) label with it and assume that it will precipitate out of solution. If everything is soluble, then no reaction will be expected.

Table $5.3.1$: Solubility Rules: Soluble Compounds and Their Exceptions

These compounds generally dissolve in water (are soluble):	Exceptions:
All compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and $NH4^+$	None
All compounds of $NO3^-$ and $C2H3O2^-$	None

Compounds of Cl^-, Br^-, I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds of SO_4^{2}	Hg_2^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}

Table 5.3.2: Solubility Rules: Insoluble Compounds and Their Exceptions

These compounds generally do not dissolve in water (are insoluble):	Exceptions:
Compounds of CO_3^{2-} and PO_4^{3-}	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+
Compounds of OH^-	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Sr^{2+}, and Ba^{2+}

For example, consider the possible double-replacement reaction between Na_2SO_4 and $SrCl_2$. The solubility rules say that all ionic sodium compounds are soluble and all ionic chloride compounds are soluble, except for Ag^+, Hg_2^{2+}, and Pb^{2+}, which are not being considered here. Therefore, Na_2SO_4 and $SrCl_2$ are both soluble. The possible double-replacement reaction products are NaCl and $SrSO_4$. Are these soluble? NaCl is (by the same rule we just quoted), but what about $SrSO_4$? Compounds of the sulfate ion are generally soluble, but Sr^{2+} is an exception: we expect it to be insoluble—a precipitate. Therefore, we expect a reaction to occur, and the balanced chemical equation would be:

$$Na_2SO_4(aq) + SrCl_2(aq) \rightarrow 2\,NaCl(aq) + SrSO_4(s)$$

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure 5.3.2).



Figure 5.3.2: Double-Replacement Reactions. Some double-replacement reactions are obvious because you can see a solid precipitate coming out of solution. Source: Photo courtesy of Choij, Wikimedia(opens in new window) [commons.wikimedia.org].

A blue solution is shown in a glass beaker. White precipitate can be seen forming at the bottom of the beaker.

Example 5.3.4:

Will a precipitation reaction occur? If so, identify the products.

1. $Ca(NO_3)_2$ + KBr → ?
2. NaOH + $FeCl_2$ → ?

Solution

1. According to the solubility rules, both $Ca(NO_3)_2$ and KBr are soluble. Now we consider what the double-replacement products would be by switching the cations (or the anions)—namely, $CaBr_2$ and KNO_3. However, the solubility rules predict that these two substances would also be soluble, so no precipitate would form. Thus, we predict no reaction in this case.

2. According to the solubility rules, both NaOH and $FeCl_2$ are expected to be soluble. If we assume that a double-replacement reaction may occur, we need to consider the possible products, which would be NaCl and $Fe(OH)_2$. NaCl is soluble, but, according to the solubility rules, $Fe(OH)_2$ is not. Therefore, a reaction would occur, and $Fe(OH)_2(s)$ would precipitate out of solution. The balanced chemical equation is

$$2\,NaOH(aq) + FeCl_2(aq) \rightarrow 2\,NaCl(aq) + Fe(OH)_2(s)$$

? Exercise 5.3.4

$$Sr(NO_3)_2 + KCl \rightarrow$$

Answer

No reaction; all possible products are soluble.

Key Takeaways

- A single-replacement reaction replaces one element for another in a compound.
- The periodic table or an activity series can help predict whether single-replacement reactions occur.
- A double-replacement reaction exchanges the cations (or the anions) of two ionic compounds.
- A precipitation reaction is a double-replacement reaction in which one product is a solid precipitate.
- Solubility rules are used to predict whether some double-replacement reactions will occur.

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5.4: Acids, Bases, and Neutralization Reactions

Learning Objectives

- Identify an acid-base neutralization reaction and predict its products.

Previously, you learned that 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.

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:

$$\text{acid} + \text{base} \rightarrow \text{water} + \text{salt}$$

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

$$\text{HCl(aq)} + \text{KOH(aq)} \rightarrow \text{H}_2\text{O}(\ell) + \text{KCl(aq)}$$

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:

$$2\,\text{HCl(aq)} + \text{Mg(OH)}_2\text{(aq)} \rightarrow 2\,\text{H}_2\text{O}(\ell) + \text{MgCl}_2\text{(aq)}$$

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.)

Example 5.4.1:

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

$$\text{HNO}_3\text{(aq)} + \text{Ba(OH)}_2\text{(aq)} \rightarrow \text{H}_2\text{O}(\ell) + \text{Ba(NO}_3\text{)}_2\text{(aq)}$$

To balance the equation, we need to realize that there will be two H_2O molecules, so two HNO_3 molecules are required:

$$2\,\text{HNO}_3\text{(aq)} + \text{Ba(OH)}_2\text{(aq)} \rightarrow 2\,\text{H}_2\text{O}(\ell) + \text{Ba(NO}_3\text{)}_2\text{(aq)}$$

This chemical equation is now balanced.

b. The expected products are water and calcium phosphate, so the initial chemical equation is

$$H_3PO_4(aq) + Ca(OH)_2(aq) \rightarrow H_2O(\ell) + Ca_3(PO_4)_2(s)$$

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:

$$2\,H_3PO_4(aq) + 3\,Ca(OH)_2(aq) \rightarrow 6\,H_2O(\ell) + Ca_3(PO_4)_2(s)$$

This chemical equation is now balanced.

? Exercise 5.4.1

Write the neutralization reaction between $H_2SO_4(aq)$ and $Sr(OH)_2(aq)$.

Answer

$$H_2SO_4(aq) + Sr(OH)_2(aq) \rightarrow 2\,H_2O(\ell) + SrSO_4(aq)$$

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:

$$3\,HCl(aq) + Fe(OH)_3(s) \rightarrow 3\,H_2O(\ell) + FeCl_3(aq)$$

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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5.5: Redox Reactions

Learning Objectives

- To identify a chemical reaction as an oxidation-reduction reaction.

When zinc metal is submerged into a quantity of aqueous HCl, the following reaction occurs (Figure $5.5.1$):

$$\mathrm{Zn(s) + 2\,HCl(aq) \rightarrow H_2(g) + ZnCl_2(aq)} \tag{5.5.1}$$

This is one example of what is sometimes called a *single replacement reaction* because Zn replaces H in combination with Cl.



Figure 5.5.1: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation 5.5.1).

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn(s) + 2\,H^+(aq) + 2\,Cl^-(aq) \rightarrow H_2(g) + Zn^{2+}(aq) + 2\,Cl^-(aq)}$$

Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing the charges on both elements.

To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called oxidation. The gain of electrons is called reduction. Because any loss of electrons by one substance must be accompanied by a gain in electrons by something else, oxidation and reduction always occur together. As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species being oxidized is called the **reducing agent**, and the species being reduced is called the **oxidizing agent**.

> *Because batteries are used as sources of electricity (that is, of electrons), all batteries are based on redox reactions.*

Although the two reactions occur together, it can be helpful to write the oxidation and reduction reactions separately as half reactions. In half reactions, we include only the reactant being oxidized or reduced, the corresponding product species, any other species needed to balance the half reaction, and the electrons being transferred. Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, in our earlier equation, now written without the chloride ions,

$$\mathrm{Zn(s) + 2\,H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)}$$

zinc atoms are oxidized to $\mathrm{Zn^{2+}}$. The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:

$$\mathrm{Zn \rightarrow Zn^{2+} + 2\,e^-}$$

This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a 2+ ion. With half reactions, there is one more item to balance: the overall charge on each side of the reaction. If you check each side of this reaction, you will note that both sides have a zero net charge.

Hydrogen is reduced in the reaction. The balanced **reduction half reaction** is as follows:

$$2\,H^+ + 2\,e^- \rightarrow H_2$$

There are two hydrogen atoms on each side, and the two electrons written as reactants serve to neutralize the 2+ charge on the reactant hydrogen ions. Again, the overall charge on both sides is zero.

The overall reaction is simply the combination of the two half reactions and is shown by adding them together.

$$\begin{array}{r} Zn \rightarrow Zn^{2+} + \cancel{2e^-} \\ \underline{2H^+ + \cancel{2e^-} \rightarrow H_2} \\ Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \end{array}$$

Because we have two electrons on each side of the equation, they can be canceled. This is the key criterion for a balanced redox reaction: the electrons have to cancel exactly. If we check the charge on both sides of the equation, we see they are the same—2+. (In reality, this positive charge is balanced by the negative charges of the chloride ions, which are not included in this reaction because chlorine does not participate in the charge transfer.)

Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel. The following example demonstrates this process.

Example 5.5.1: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Solution

We start by using symbols of the elements and ions to represent the reaction:

$$Ag^+ + Al \rightarrow Ag + Al^{3+}$$

The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag^+ to Ag:

Reduction half-reaction:

$$Ag^+ + e^- \rightarrow Ag$$

Aluminum is oxidized, losing three electrons to change from Al to Al^{3+}:

Oxidation half-reaction:

$$Al \rightarrow Al^{3+} + 3\,e^-$$

To combine these two half reactions and cancel out all the electrons, we need to multiply the silver reduction reaction by 3:

$$\begin{array}{r} 3\left(Ag^+ + e^- \rightarrow Ag\right) \\ \underline{Al \rightarrow Al^{3+} + 3e^-} \\ 3Ag^+ + Al \rightarrow 3Ag + Al^{3+} \end{array}$$

Now the equation is balanced, not only in terms of elements but also in terms of charge.

- The **substance oxidized** is the reactant that had undergone oxidation: Al
- The **substance reduced** is the reactant that had undergone reduction: Ag^+
- The **reducing agent** is the same as the substance oxidized: Al
- The **oxidizing agent** is the same as the substance reduced: Ag^+

Exercise 5.5.1

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Answer

Reduction: $Ca^{2+} + 2e^- \rightarrow Ca$

Oxidation: $2\ (K \rightarrow K^+ + e^-)$

Combined: $Ca^{2+} + 2K \rightarrow Ca + 2K^+$

- The **substance oxidized** is the reactant that had undergone oxidation: K
- The **substance reduced** is the reactant that had undergone reduction: Ca^{2+}
- The **reducing agent** is the same as the substance oxidized: K
- The **oxidizing agent** is the same as the substance reduced: Ca^{2+}

Potassium has been used as a reducing agent to obtain various metals in their elemental form.

To Your Health: Redox Reactions and Pacemaker Batteries

All batteries use redox reactions to supply electricity because electricity is basically a stream of electrons being transferred from one substance to another. Pacemakers—surgically implanted devices for regulating a person's heartbeat—are powered by tiny batteries, so the proper operation of a pacemaker depends on a redox reaction.

Pacemakers used to be powered by NiCad batteries, in which nickel and cadmium (hence the name of the battery) react with water according to this redox reaction:

$$\mathrm{Cd(s) + 2\,NiOOH(s) + 2\,H_2O(\ell) \rightarrow Cd(OH)_2(s) + 2\,Ni(OH)2\ (s)}$$

The cadmium is oxidized, while the nickel atoms in NiOOH are reduced. Except for the water, all the substances in this reaction are solids, allowing NiCad batteries to be recharged hundreds of times before they stop operating. Unfortunately, NiCad batteries are fairly heavy batteries to be carrying around in a pacemaker. Today, the lighter lithium/iodine battery is used instead. The iodine is dissolved in a solid polymer support, and the overall redox reaction is as follows:

$$\mathrm{2\,Li(s) + I_2(s) \rightarrow 2\,LiI(s)}$$

Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace the pacemaker/battery unit. Lithium/iodine batteries are also used to power calculators and watches.



Figure 5.5.1: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

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).

$$\mathrm{2\,CH_3CHO + O_2 \rightarrow 2\,CH_3COOH}$$

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:

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$$

Table 5.5.1: Oxidation-Reduction Reactions and the Changes in Oxygen and Hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

Example 5.5.2

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 5.5.2

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.

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5.6: Recognizing Redox Reactions

Learning Objectives

- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.
2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.
3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number (except in peroxide compounds [where it is −1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a +1 oxidation number (except when it exists as the hydride ion [H^-], in which case rule 2 prevails).
4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).

Here are some examples for practice. In H_2, both H atoms have an oxidation number of 0 by rule 1. In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1 by rule 2. In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1. We can use rule 4 to determine oxidation numbers for the atoms in SO_2. Each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

Example 5.6.1

Assign oxidation numbers to the atoms in each substance.

1. Cl_2
2. GeO_2
3. $Ca(NO_3)_2$

Solution

1. Cl_2 is the elemental form of chlorine. Rule 1 states each atom has an oxidation number of 0.
2. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
3. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation $x + 3(-2) = -1$

   where x is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for x,

   $x + (-6) = -1x = +5$

   Thus the oxidation number on the N atom in the NO_3^- ion is +5.

? Exercise 5.6.1: Phosphoric Acid

Assign oxidation numbers to the atoms in H_3PO_4.

Answer

H: +1; O: −2; P: +5

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

✔ Example 5.6.2:

Identify what is being oxidized and reduced in this redox reaction.

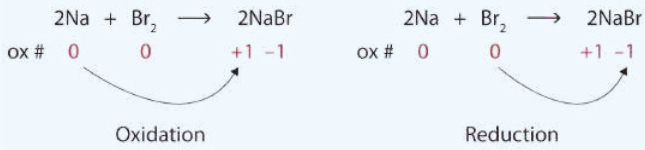
$$2\,\mathrm{Na} + \mathrm{Br_2} \rightarrow 2\,\mathrm{NaBr}$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of −1.

$$\underset{0}{2Na} + \underset{0}{Br_2} \rightarrow \underset{+1-1}{2NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Because oxidation numbers 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).

? Exercise 5.6.2

Identify what is being oxidized and reduced in this redox reaction.

$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}$$

Answer

C is being oxidized from 0 to +4; O is being reduced from 0 to −2.

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6H^+(aq) + 2\underset{+7}{MnO_4^-}(aq) + 5\underset{-1}{H_2O_2}(l) \rightarrow 2\underset{+2}{Mn^{2+}}(aq) + 5\underset{0}{O_2}(g) + 8H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced?

Food and Drink Application: Fortifying Food with Iron

Iron is an essential mineral in our diet; iron-containing compounds like the heme protein in hemoglobin could not function without it. Most biological iron has the form of the Fe^{2+} ion; iron with other oxidation numbers is almost inconsequential in human biology (although the body does contain an enzyme to reduce Fe^{3+} to Fe^{2+}, so Fe^{3+} must have some biological significance, albeit minor). To ensure that we ingest enough iron, many foods are enriched with iron. Although Fe^{2+} compounds are the most logical substances to use, some foods use "reduced iron" as an ingredient (bread and breakfast cereals are the most well-known examples). Reduced iron is simply iron metal; iron is added as a fine metallic powder. The metallic iron is oxidized to Fe^{2+} in the digestive system and then absorbed by the body, but the question remains: Why are we ingesting metallic iron? Why not just use Fe^{2+} salts as an additive?



Figure 5.6.1 Ingredients. Many prepared foods list reduced iron in their ingredients list.

The ingredients list contains Flour (Contains: wheat flour, malted barley flour, niacin, reduced iron, thiamine mononitrate, riboflavin, folic acid), water, sourdough (6.4%) (contains: water, flour [wheat flour, malted barley flour, niacin, reduced iron, thiamine mononitrate, riboflavin, folic acid], yeast), salt, wheat germ, semolina (contains: durum wheat semolina, niacin, ferrous sulphate, thiamine mononitrate, riboflavin, folic acid).

Although it is difficult to establish conclusive reasons, a search of scientific and medical literature suggests a few reasons. One reason is that fine iron filings do not affect the taste of the product. The size of the iron powder (several dozen micrometers) is not noticeable when chewing iron-supplemented foods, and the tongue does not detect any changes in flavor that can be detected when using Fe^{2+} salts. Fe^{2+} compounds can affect other properties of foodstuffs during preparation and cooking, like dough pliability, yeast growth, and color. Finally, of the common iron substances that might be used, metallic iron is the least expensive. These factors appear to be among the reasons why metallic iron is the supplement of choice in some foods.

Key Takeaways

- Oxidation numbers are used to keep track of electrons in atoms.
- There are rules for assigning oxidation numbers to atoms.
- Oxidation is an increase in oxidation number (loss of electrons); reduction is a decrease in oxidation number (gain of electrons).

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5.7: Net Ionic Equations

Learning Objectives

- Write ionic and net ionic equations for chemical reactions involving ions.

At sports events around the world, a small number of athletes fiercely compete on fields and in stadiums. They get tired, dirty, and sometimes hurt as they try to win the game. Surrounding them are thousands of spectators watching and cheering. Would the game be different without the spectators? Definitely! Spectators provide encouragement to the team and generate enthusiasm. Although the spectators are not playing the game, they are certainly a part of the process.

Net Ionic Equations

We can write a molecular equation for the formation of silver chloride precipitate:

$$\mathrm{NaCl} + \mathrm{AgNO_3} \rightarrow \mathrm{NaNO_3} + \mathrm{AgCl}$$

The corresponding **ionic equation** is written to show the *ions* that are dissolved in solution:

$$\mathrm{Na^+}\,(aq) + \mathrm{Cl^-}\,(aq) + \mathrm{Ag^+}\,(aq) + \mathrm{NO_3^-}\,(aq) \rightarrow \mathrm{Na^+}\,(aq) + \mathrm{NO_3^-}\,(aq) + \mathrm{AgCl}\,(s)$$

If you look carefully at the ionic equation, you will notice that the sodium ion and the nitrate ion appear unchanged on both sides of the equation. When the two solutions are mixed, neither the $\mathrm{Na^+}$ nor the $\mathrm{NO_3^-}$ ions participate in the reaction. They can be eliminated from the reaction.

$$\cancel{\mathrm{Na^+}\,(aq)} + \mathrm{Cl^-}\,(aq) + \mathrm{Ag^+}\,(aq) + \cancel{\mathrm{NO_3^-}\,(aq)} \rightarrow \cancel{\mathrm{Na^+}\,(aq)} + \cancel{\mathrm{NO_3^-}\,(aq)} + \mathrm{AgCl}\,(s)$$

A **spectator ion** is an ion that does not take part in the chemical reaction and is found in solution both before and after the reaction. In the above reaction, the sodium ion and the nitrate ion are both spectator ions. The equation can now be written without the spectator ions:

$$\mathrm{Ag^+}\,(aq) + \mathrm{Cl^-}\,(aq) \rightarrow \mathrm{AgCl}\,(s)$$

The **net ionic equation** is the chemical equation that shows only those elements, compounds, and ions that are directly involved in the chemical reaction. Notice that in writing the net ionic equation, the positively-charged silver cation was written first on the reactant side, followed by the negatively-charged chloride anion. This is somewhat customary because that is the order in which the ions must be written in the silver chloride product. However, it is not absolutely necessary to order the reactants in this way.

Net ionic equations must be balanced by both mass and charge. Balancing by mass means ensuring that there are equal masses of each element on the product and reactant sides. Balancing by charge means making sure that the overall charge is the same on both sides of the equation. In the above equation, the overall charge is zero, or neutral, on both sides of the equation. As a general rule, if you balance the molecular equation properly, the net ionic equation will end up being balanced by both mass and charge.

5.7.1 Example

When aqueous solutions of copper (II) chloride and potassium phosphate are mixed, a precipitate of copper (II) phosphate is formed. Write a balanced net ionic equation for this reaction.

Solution

Step 1: Plan the problem.

Write and balance the molecular equation first, making sure that all formulas are correct. Then write the ionic equation, showing all aqueous substances as ions. Carry through any coefficients. Finally, eliminate spectator ions and write the net ionic equation.

Step 2: Solve.

Molecular equation:

$$3\mathrm{CuCl_2}\,(aq) + 2\mathrm{K_3PO_4}\,(aq) \rightarrow 6\mathrm{KCl}\,(aq) + \mathrm{Cu_3(PO_4)_2}\,(s)$$

Ionic equation:

$$3Cu^{2+}(aq) + 6Cl^{-}(aq) + 6K^{+}(aq) + 2PO_4^{3-}(aq) \rightarrow 6K^{+}(aq) + 6Cl^{-}(aq) + Cu_3(PO_4)_2(s)$$

Notice that the balance of the equation is carried through when writing the dissociated ions. For example, there are six chloride ions on the reactant side because the coefficient of 3 is multiplied by the subscript of 2 on the copper (II) chloride formula. The spectator ions, K^{+} and Cl^{-}, can be eliminated.

Net ionic equation:

$$3Cu^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Cu_3(PO_4)_2(s)$$

Step 3: Think about your result.

For a precipitation reaction, the net ionic equation always shows the two ions that come together to form the precipitate. The equation is balanced by mass and charge.

Summary

- A spectator ion is an ion that does not take part in the chemical reaction and is found in solution both before and after the reaction.
- The net ionic equation is the chemical equation that shows only those elements, compounds, and ions that are directly involved in the chemical reaction.
- An example of writing a net ionic equation is outlined.

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CHAPTER OVERVIEW

6: Chemical Reactions - Mole and Mass Relationships

6.1: The Mole and Avogadro’s Number
6.2: Gram-Mole Conversions
6.3: Mole Relationships and Chemical Equations
6.4: Mass Relationships and Chemical Equations
6.5: Limiting Reagent and Percent Yield

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6.1: The Mole and Avogadro's Number

Learning Objectives

- Calculate formula masses for covalent and ionic compounds.
- Define the amount unit mole and the related quantity Avogadro's number.
- Calculate molar mass of a compound from the molecular formula.

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

Formula Mass

In an earlier chapter, we described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the **formula mass** of a substance, which is equal to the sum of the atomic masses for all the atoms represented in the substance's formula.

Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure 6.1.1 outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37

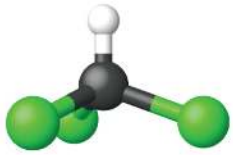


Figure 6.1.1: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: "Element," "Quantity," a blank space, "Average atomic mass (a m u)," a blank space, and "Subtotal (a m u)." The first column contains the symbols "C," "H," "C l" and a blank, merged cell that runs the width of the first five columns. The second column contains the numbers "1," "1," and "3" as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers "12.01," "1.008," and "35.45" as well as the merged cell. The fifth column contains the symbol "=" in each cell except for the last, merged cell. The sixth column contains the values "12.01," "1.008," "106.35," and "119.37." There is a thick black line below the number 106.35. The merged cell under the first five columns reads "Molecular mass." To the left of the table is a diagram of a molecule. Three green spheres are attached to a slightly smaller black sphere, which is also attached to a smaller white sphere. The green spheres lie beneath and to the sides of the black sphere while the white sphere is located straight up from the black sphere.

Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu (Figure 6.1.2).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15

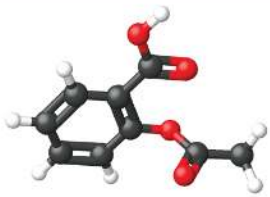


Figure 6.1.2: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “9,” “8,” and “4” as well as the merged, cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” and “16.00” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values: “108.09,” “8.064,” “64.00,” and “180.15.” There is a thick black line below the number 64.00. The merged cell under the first five columns reads “Molecular mass.” To the left of the table is a diagram of a molecule. Six black spheres are located in a six-sided ring and connected by alternating double and single black bonds. Attached to each of the four black spheres is one smaller white sphere. Attached to the farthest right black sphere is a red sphere, connected to two more black spheres, all in a row. Attached to the last black sphere of that row are two more white spheres. Attached to the first black sphere of that row is another red sphere. A black sphere, attached to two red spheres and a white sphere is attached to the black sphere on the top right of the six-sided ring.

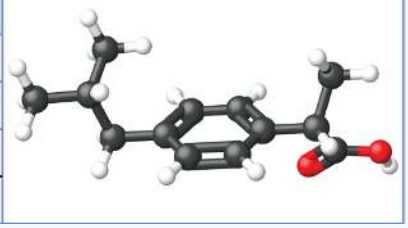
✔ Example 6.1.1: Computing Molecular Mass for a Covalent Compound

Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

Solution

Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.114
O	2	×	16.00	=	32.00
				Molecular mass	206.27



? Exercise 6.1.1

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

Answer

151.16 amu

Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound’s formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the “molecular mass.”

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is

computed as 58.44 amu (Figure 6.1.3).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

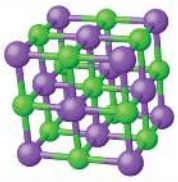


Figure 6.1.3: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space and “Subtotal (a m u).” The first column contains the symbols “N a”, “C l,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “1” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “22.99” and “35.45” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “22.99,” “35.45,” and “58.44.” There is a thick black line below the number “35.45.” The merged cell under the first five columns reads “Formula mass.” To the left of the table is a diagram of a chemical structure. The diagram shows green and purple spheres placed in an alternating pattern, making up the corners of eight stacked cubes to form one larger cube. The green spheres are slightly smaller than the purple spheres.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

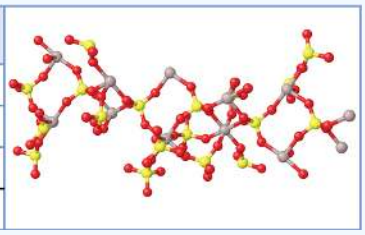
✔ Example 6.1.2: Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14



? Exercise 6.1.2

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

Answer

310.18 amu

The Mole

So far, we have been talking about chemical substances in terms of individual atoms and molecules. Yet we do not typically deal with substances one atom or molecule at a time; we work with millions, billions, and trillions of atoms and molecules at a time. We need a way to deal with macroscopic, rather than microscopic, amounts of matter. We need a unit of amount that relates quantities of substances on a scale that we can interact with.

Chemistry uses a unit called **mole**. The mole (mol) is an counting term similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. A mole is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word "mole" is "large mass" or "bulk," which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

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

How big is a mole? It is very large. Suppose you had a mole of dollar bills that need to be counted. If everyone on earth (about 6 billion people) counted one bill per second, it would take about 3.2 million years to count all the bills. A mole of sand would fill a cube about 32 km on a side. A mole of pennies stacked on top of each other would have about the same diameter as our galaxy, the Milky Way. Atoms and molecules are very tiny, so one mole of carbon atoms would make a cube that is 1.74 cm on a side, small enough to carry in your pocket. One mole of water molecules is approximately 18 mL or just under 4 teaspoons of water.

Example 6.1.3

How many molecules are present in 2.76 mol of H_2O? How many atoms is this?

Solution

The definition of a mole is an equality that can be used to construct a conversion factor. Also, because we know that there are three atoms in each molecule of H_2O, we can also determine the number of atoms in the sample.

$$2.76\ \cancel{mol\ H_2O} \times \frac{6.022 \times 10^{23} molecules\ H_2O}{\cancel{mol\ H_2O}} = 1.66 \times 10^{24} molecules\ H_2O$$

To determine the total number of atoms, we have

$$1.66 \times 10^{24}\ \cancel{molecules\ H_2O} \times \frac{3\ atoms}{1\ molecule} = 4.99 \times 10^{24}\ atoms$$

Exercise 6.1.3

How many molecules are present in 4.61×10^{-2} mol of O_2?

Answer

2.78×10^{22} molecules

Molar Mass

Why is the mole unit so important? It represents the link between the microscopic and the macroscopic, especially in terms of mass. *A mole of a substance has the same mass in grams as one unit (atom or molecules) has in atomic mass units*. The mole unit allows us to express amounts of atoms and molecules in visible amounts that we can understand.

For example, we already know that, by definition, a mole of carbon has a mass of exactly 12 g. This means that exactly 12 g of C has 6.022×10^{23} atoms:

$$12\ g\ C = 6.022 \times 10^{23}\ atoms\ C$$

We can use this equality as a conversion factor between the number of atoms of carbon and the number of grams of carbon. How many grams are there, say, in 1.50×10^{25} atoms of carbon? This is a one-step conversion:

$$1.50 \times 10^{25}\ \cancel{atoms\ C} \times \frac{12.0000\ g\ C}{6.022 \times 10^{23}\ \cancel{atoms\ C}} = 299\ g\ C$$

But it also goes beyond carbon. Previously we defined atomic and molecular masses as the number of atomic mass units per atom or molecule. Now we can do so in terms of grams. The atomic mass of an element is the number of grams in 1 mol of atoms of that element, while the molecular mass of a compound is the number of grams in 1 mol of molecules of that compound. Sometimes these masses are called **molar masses** to emphasize the fact that they are the mass for 1 mol of things. (The term *molar* is the adjective form of mole and has nothing to do with teeth.)

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (Figure 6.1.1).

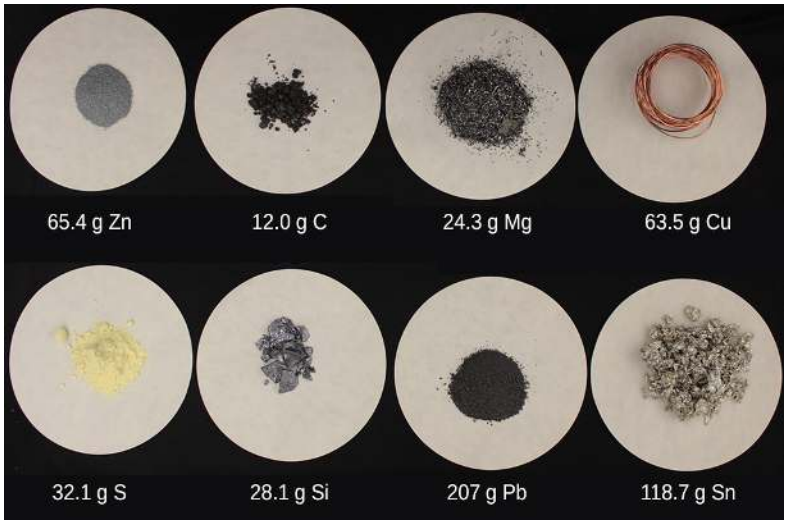


Figure 6.1.1: Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

This figure contains eight different substances displayed on white circles. The amount of each substance is visibly different.

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

Table 6.1.1: Mass of one mole of elements

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

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the

mole, consider a small drop of water after a rainfall. Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.



Video 6.1.1: The mole is used in chemistry to represent 6.022×10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this video and then complete the "Think" questions that follow. Explore more about the mole by reviewing the information under "Dig Deeper."

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

Here are some examples. The mass of 1 hydrogen atom is 1.0079 u; the mass of 1 mol of hydrogen atoms is 1.0079 g. Elemental hydrogen exists as a diatomic molecule, H_2. One molecule has a mass of 1.0079 u + 1.0079 u = 2.0158 u, while 1 mol of H_2 has a mass of 1.0079 g + 1.0079 g = 2.0158 g. One molecule of H_2O has a mass of about 18.01 u; 1 mol H_2O has a mass of 18.01 g. A single unit of NaCl has a mass of 58.45 u; NaCl has a molar mass of 58.45 g. In each of these moles of substances, there are 6.022×10^{23} units: 6.022×10^{23} atoms of H, 6.022×10^{23} molecules of H_2 and H_2O, 6.022×10^{23} units of NaCl ions. These relationships give us plenty of opportunities to construct conversion factors for simple calculations.

✔ ✔ Example 6.1.4: Sugar

What is the molar mass of sugar ($C_6H_{12}O_6$)?

Solution

To determine the molar mass, we simply add the atomic masses of the atoms in the molecular formula; but express the total in grams per mole, not atomic mass units. The masses of the atoms can be taken from the periodic table.

6 C = 6 × 12.011	= 72.066
12 H = 12 × 1.0079	= 12.0948
6 O = 6 × 15.999	= 95.994
TOTAL	= 180.155 g/mol

Per convention, the unit *grams per mole* is written as a fraction.

? Exercise 6.1.4

What is the molar mass of $AgNO_3$?

Answer

169.87 g/mol

Summary

The mole is a key unit in chemistry. The molar mass of a substance, in grams, is numerically equal to one atom's or molecule's mass in atomic mass units.

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6.2: 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).

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 6.2.1). 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:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \quad \text{and} \quad \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

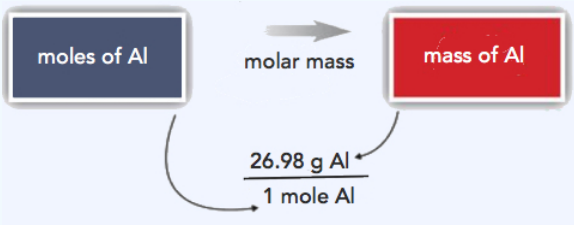
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

Example 6.2.1

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.

Exercise 6.2.1

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

$$100.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 3.706 \text{ mol Al}$$

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 6.2.1 is a chart for determining what conversion factor is needed, and Figure 6.2.2 is a flow diagram for the steps needed to perform a conversion.

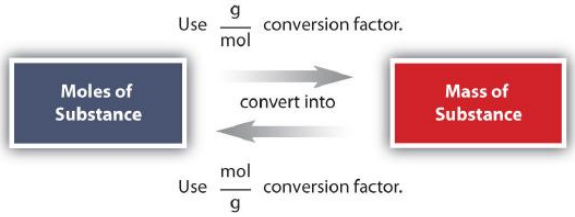


Figure 6.2.1 A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

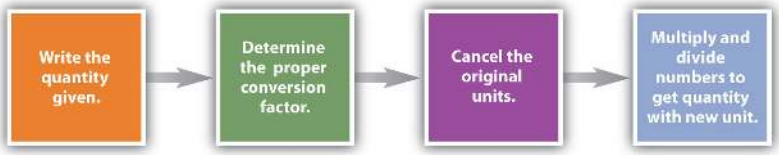


Figure 6.2.2 A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

Example 6.2.2

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 6.2.2:

$$0.00655 \text{ mol bilirubin} \times \frac{584.73 \text{ g bilirubin}}{\text{mol bilirubin}} = 3.83 \text{ g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

Exercise 6.2.2

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 6.2.1: 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	6.7×10^{-7} mol	25 µg	4.8×10^{-7} mol
Cu	900 µg	1.4×10^{-5} mol	900 µg	1.4×10^{-5} mol
F	4 mg	2.1×10^{-4} mol	3 mg	1.5×10^{-4} mol
I	150 µg	1.2×10^{-6} mol	150 µg	1.2×10^{-6} mol
Fe	8 mg	1.4×10^{-4} mol	18 mg	3.2×10^{-4} mol
K	3,500 mg	9.0×10^{-2} mol	3,500 mg	9.0×10^{-2} mol
Mg	400 mg	1.6×10^{-2} mol	310 mg	1.3×10^{-2} mol
Mn	2.3 mg	4.2×10^{-5} mol	1.8 mg	3.3×10^{-5} mol
Mo	45 mg	4.7×10^{-7} mol	45 mg	4.7×10^{-7} mol
Na	2,400 mg	1.0×10^{-1} mol	2,400 mg	1.0×10^{-1} mol
P	700 mg	2.3×10^{-2} mol	700 mg	2.3×10^{-2} mol
Se	55 µg	7.0×10^{-7} mol	55 µg	7.0×10^{-7} mol
Zn	11 mg	1.7×10^{-4} mol	8 mg	1.2×10^{-4} mol

Table 6.2.1 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*).

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6.3: 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.

Consider the simple chemical equation

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

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

$$4\,H_2 + 2\,O_2 \rightarrow 4\,H_2O$$

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

$$22\,H_2 + 11\,O_2 \rightarrow 22\,H_2O$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$

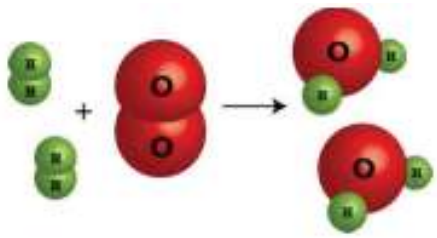
These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ \text{mol}\ H_2 + 1\ \text{mol}\ O_2 \rightarrow 2\ \text{mol}\ H_2O$$

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

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

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 6.3.1: 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.**

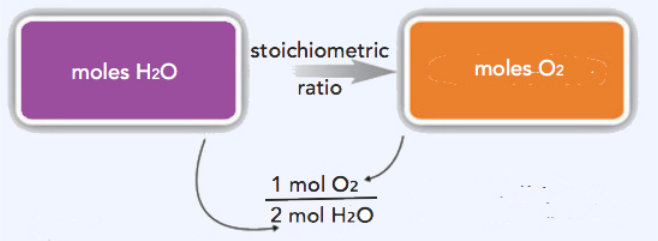
Example 6.3.1

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 6.3.1

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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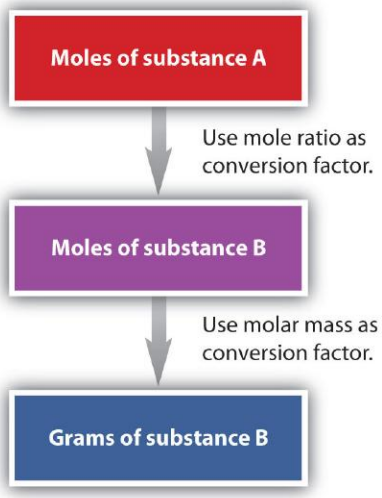
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6.4: Mass Relationships and Chemical Equations

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. 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

$$\mathrm{Fe_2O_3} + 3\,\mathrm{SO_3} \rightarrow \mathrm{Fe_2(SO_4)_3}$$

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:

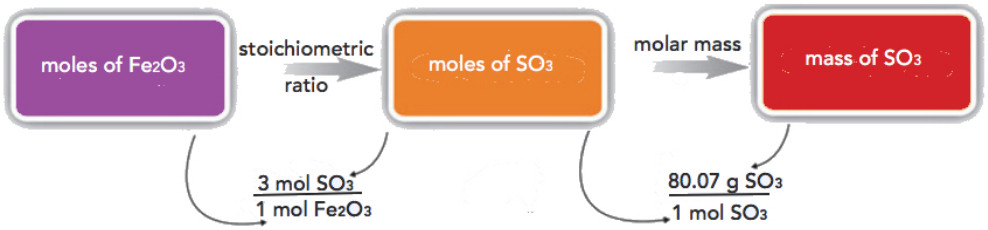
$$3.59\ \text{mol}\ \mathrm{Fe_2O_3} \times \frac{3\ \text{mol}\ \mathrm{SO_3}}{1\ \text{mol}\ \mathrm{Fe_2O_3}} = 10.77\ \text{mol}\ \mathrm{SO_3}$$

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:

$$10.77\ \text{mol}\ \mathrm{SO_3} \times \frac{80.07\ \text{g}\ \mathrm{SO_3}}{1\ \text{mol}\ \mathrm{SO_3}} = 862.4\ \text{g}\ \mathrm{SO_3}$$

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 6.4.1

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

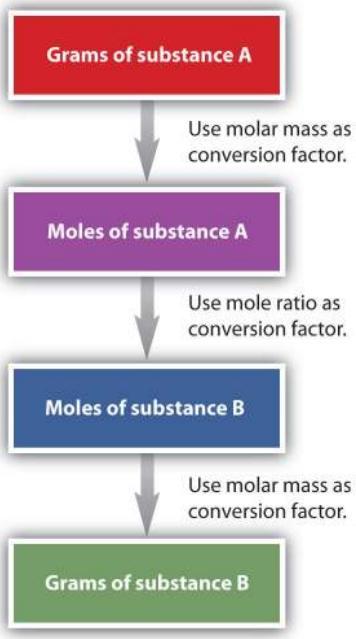
How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of H_2O are reacted according to this balanced chemical equation?

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2$$

Answer

$$17.3 \text{ mol } H_2O \times \frac{1 \text{ mol } C_6H_{12}O_6}{6 \text{ mol } H_2O} \times \frac{180.18 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6} = 520 \text{ g } C_6H_{12}O_6$$

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 6.4.2: 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 CH_4?

Solution

First, let us work the problem in stepwise fashion. We begin by converting the mass of CH_4 to moles of CH_4, using the molar mass of CH_4 (16.05 g/mol) as the conversion factor:

$$100.0\text{ g } CH_4 \times \frac{1\text{ mol } CH_4}{16.05\text{ g } CH_4} = 6.231\text{ mol } CH_4$$

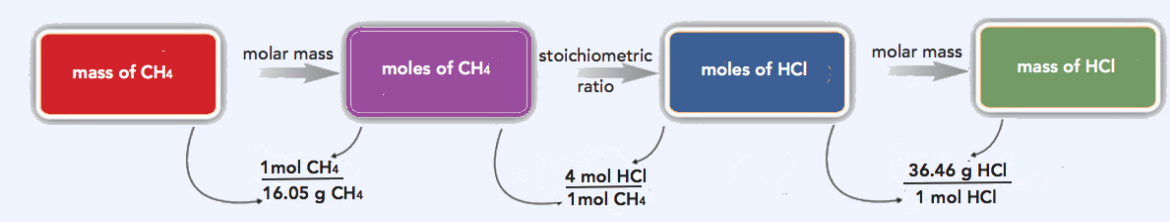
Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles CCl_4 and moles HCl and convert our first result into moles of HCl:

$$6.231\text{ mol } CH_4 \times \frac{4\text{ mol HCl}}{1\text{ mol } CH_4} = 24.92\text{ mol HCl}$$

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:

$$24.92\text{ mol HCl} \times \frac{36.46\text{ g HCl}}{1\text{ mol HCl}} = 908.5\text{ g HCl}$$

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 6.4.2: 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

$$135.8 \text{ g } K_2Cr_2O_7 \times \frac{1 \text{ mol } K_2Cr_2O_7}{294.20 \text{ g } K_2Cr_2O_7} \times \frac{1 \text{ mol } CH_3CH_2COOH}{2 \text{ mol } K_2Cr_2O_7} \times \frac{74.09 \text{ g } CH_3CH_2COOH}{1 \text{ mol } CH_3CH_2COOH} = 17.10 \text{ g } CH_3CH_2COOH$$

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.

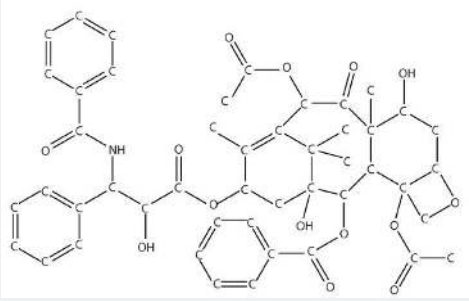


Figure 6.4.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

Key Takeaway

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

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6.5: 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

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{6.5.1}$$

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 6.5.1:

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?

$$\mathrm{Zn(s) + 2\,HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2(g)}$$

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:

$$30.5\ g\ \cancel{Zn} \times \frac{1\ \cancel{mol\ Zn}}{65.39\ g\ \cancel{Zn}} \times \frac{1\ \cancel{mol\ Zn(NO_3)_2}}{1\ \cancel{mol\ Zn}} \times \frac{189.41\ g\ Zn(NO_3)_2}{1\ \cancel{mol\ Zn(NO_3)_2}} = 88.3\ g\ Zn(NO_3)_2$$

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 6.5.1):

$$\frac{65.2\ g\ Zn(NO_3)_2}{88.3\ g\ Zn(NO_3)_2} \times 100\% = 73.8\%$$

The worker achieved almost three-fourths of the possible yield.

Exercise 6.5.1

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 6.5.1 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

$$1\ \text{box mix} + 2\ \text{eggs} \rightarrow 1\ \text{batch brownies} \tag{6.5.2}$$

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.

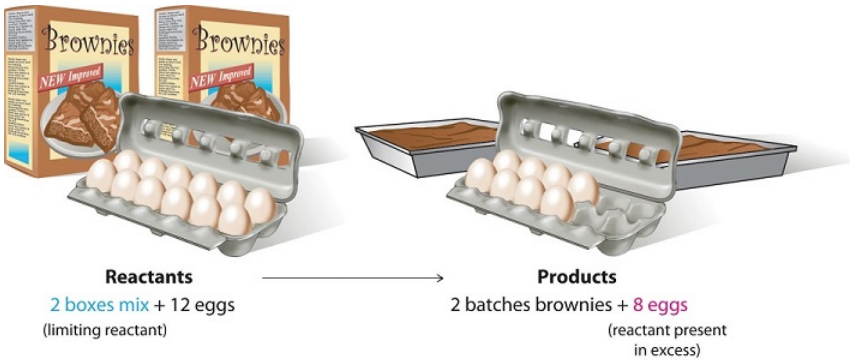


***Figure* 6.5.1**: *The Concept of a Limiting Reactant in the Preparation of Brownies*

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:

$$50.0\ g\ As \times \frac{1\ mol\ As}{74.92\ g\ As} \times \frac{2\ mol\ As_2O_3}{4\ mol\ As} = 0.334\ mol\ As_2O_3$$

$$50.0\ g\ O_2 \times \frac{1\ mol\ O_2}{32.00\ g\ O_2} \times \frac{2\ mol\ As_2O_3}{3\ mol\ O_2} = 1.04\ mol\ As_2O_3$$

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

$$0.334\ mol\ As_2O_3 \times \frac{197.84\ g\ As_2}{1\ mol\ As_2O_3} = 66.1\ g\ As_2O_3$$

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,

$$50.0\ g\ As \times \frac{1\ mol\ As}{74.92\ g\ As} \times \frac{3\ mol\ O_2}{4\ mol\ As} \times \frac{32.00\ g\ O_2}{1\ mol\ O_2} = 16.0\ g\ O_2\ reacted$$

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 6.5.1:

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.

$$5.00\ g\ Rb \times \frac{1\ mol\ Rb}{85.47\ g\ Rb} \times \frac{1\ mol\ Mg}{2\ mol\ Rb} \times \frac{24.31\ g\ Mg}{1\ mol\ Mg} = 0.711\ g\ Mg$$

$$3.44\ g\ \cancel{MgCl_2} \times \frac{1\ \cancel{mol\ MgCl_2}}{95.21\ g\ \cancel{MgCl_2}} \times \frac{1\ \cancel{mol\ Mg}}{1\ \cancel{mol\ MgCl_2}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.878\ g\ Mg$$

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.

$$5.00\ g\ \cancel{Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ g\ \cancel{Rb}} \times \frac{1\ \cancel{mol\ MgCl_2}}{2\ \cancel{mol\ Rb}} \times \frac{95.21\ g\ Mg}{1\ \cancel{mol\ MgCl_2}} = 2.78\ g\ MgCl_2\ \ reacted$$

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 6.5.1

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

7: Chemical Reactions - Energy, Rates, and Equilibrium

7.1: Energy and Chemical Bonds
7.2: Heat Changes during Chemical Reactions
7.3: Exothermic and Endothermic Reactions
7.4: Why Do Chemical Reactions Occur? Free Energy
7.5: How Do Chemical Reactions Occur? Reaction Rates
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
7.7: Reversible Reactions and Chemical Equilibrium
7.8: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria

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7.1: Energy and Chemical Bonds

Learning Objectives

- Define energy and distinguish the different types of energy, potential and kinetic.

Chemical changes and their accompanying changes in *energy* are important parts of our everyday world (Figure 7.1.1). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a) (b) (c)

Figure 7.1.1: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by “Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, often referred to as *stored energy*, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 7.1.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure 7.1.2: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. **Heat** is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

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7.2: Heat Changes during Chemical Reactions

Learning Objectives

- Define *bond dissociation energy*.
- Determine if a chemical process is exothermic or endothermic.

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 Dissociation Energy

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 by putting energy into a molecule, which causes its bonds to break, separating the molecule into individual atoms. Bonds between certain specific elements usually have a characteristic energy, called the **bond dissociation 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 dissociation 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 dissociation 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 dissociation energy of a C–H bond as being about 100 kcal/mol. Table 7.2.1 lists the approximate bond dissociation energies of various covalent bonds.

Table 7.2.1: Approximate Bond Dissociation Energies

Bond	Bond Dissociation 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

Bond	Bond Dissociation Energy (kcal/mol)
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 energy change, for a given reaction can be calculated using the bond dissociation energy values from Table 7.2.1.

Enthalpy Change or Heat of Reaction, Δ*H*

During a chemical reaction, bonds are broken and new bonds are formed. Breaking chemical bonds is **endothermic**, a process that requires an input of energy or absorption of heat. The reverse process of bond breaking is bond formation, which is **exothermic**, meaning it releases energy or gives off heat. The bond dissociation energy values listed in the above table give the amount of energy required to break a specific bond. When that same bond is reformed, an identical amount of energy is released. The numerical *value* of energy is the same for breaking and forming a bond, but the sign, or *direction* of the process is different. The overall energy change of a specific bond breaking and reforming would be zero, in other words energy is neither created or destroyed, following the law of conservation of energy.

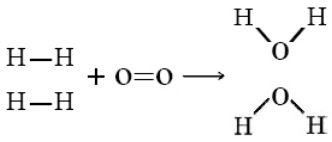
In a chemical reaction, the bonds breaking are often different than the bonds reforming, sometimes there is more heat absorbed (more bonds are broken) and sometimes more heat is released (more bonds are formed). The measured *difference* between the total heat absorbed and the total heat released during a chemical reaction (performed at constant pressure) is called the **heat of reaction** or **enthalpy change**, and is represented by the symbol Δ*H* (where the Δ stands for change and the H represents enthalpy).

$$\text{enthalpy change} \approx \Sigma\ (\text{bond dissociation energies}_{reactants}) - \Sigma\ (\text{bond dissociation energies}_{products}) \qquad (7.2.1)$$

The ≈ sign is used because we are adding together *average* bond dissociation energies; 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:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad (7.2.2)$$



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 from the reactant side are broken, while 4 O–H bonds (two for each H_2O) are formed on the product side. The energy changes can be tabulated and calculated as follows:

Reactant Bond Dissociation Energy (kcal/mol)		Product Bond Dissociation Energy (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

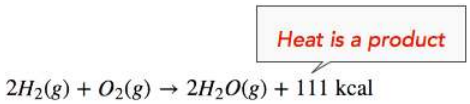
$$\Delta H \approx \Sigma\ (\text{bond dissociation energies}_{reactants}) - \Sigma\ (\text{bond dissociation energies}_{products}) \qquad (7.2.3)$$

$$\Delta H \approx 329\ \text{kcal} - 440\ \text{kcal} \qquad (7.2.4)$$

$$\Delta H \approx -111\ \text{kcal} \qquad (7.2.5)$$

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 absorbs. This excess energy is **released** as heat, so the reaction is **exothermic**. 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.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad \Delta H = -111\ \text{kcal} \tag{7.2.6}$$

Example 7.2.1

What is the enthalpy change for this reaction? Is the reaction exothermic or endothermic?

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g) \tag{7.2.7}$$

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 dissociation energies of these bonds from Table 7.2.1:

- 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.

Reactant Bond Dissociation Energy (kcal/mol)		**Product Bond Dissociation Energy (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

$$\Delta H \approx 151\ \text{kcal} - 174\ \text{kcal} \tag{7.2.8}$$

$$\Delta H \approx -23\ \text{kcal} \tag{7.2.9}$$

Step 5- Since Δ*H* is negative (−23 kcal), the reaction is *exothermic*.

Exercise 7.2.1

Using the bond dissociation energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \tag{7.2.10}$$

Is the reaction written above exothermic or endothermic? Explain.

Answer

Δ*H* = −43 kcal

Since Δ*H* is negative (−43 kcal), the reaction is *exothermic*.

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7.3: Exothermic and Endothermic Reactions

Learning Objectives

- Use bond dissociation energies to calculate enthalpy change or heat of reaction.
- Determine if a chemical process is exothermic or endothermic.

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 (ΔH 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 (ΔH 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 7.3.1.

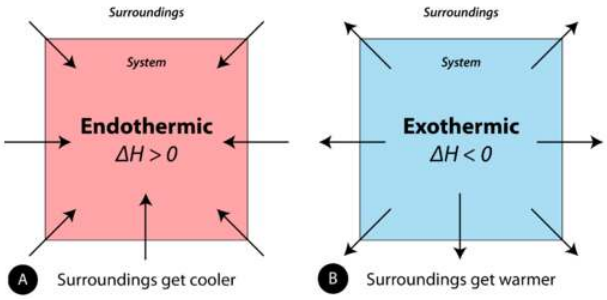
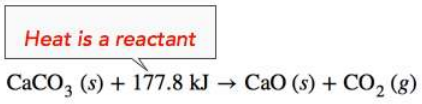


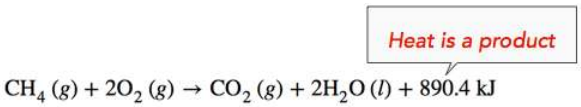
Figure 7.3.1: (A) Endothermic reaction. (B) Exothermic reaction.

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 ΔH is *positive* for an endothermic reaction.



$$\mathrm{CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)} \quad \Delta H = +177.8\ \mathrm{kJ} \tag{7.3.1}$$

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 ΔH information with a *negative* sign, -890.4 kJ.



$$\mathrm{CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)} \quad \Delta H = -890.4\ \mathrm{kJ} \tag{7.3.2}$$

Example 7.3.1

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 7.3.1

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 7.3.2. 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 7.3.2*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 7.3.2*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.

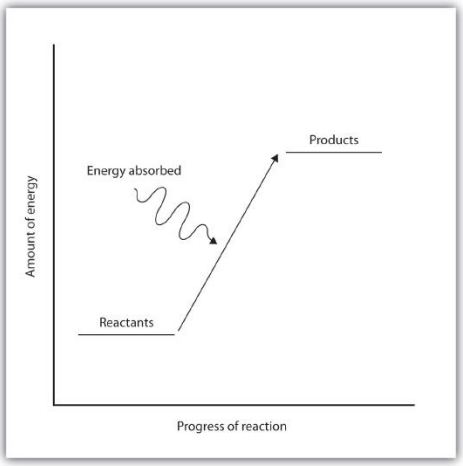


Figure 7.3.2*A*: Endothermic Reactions

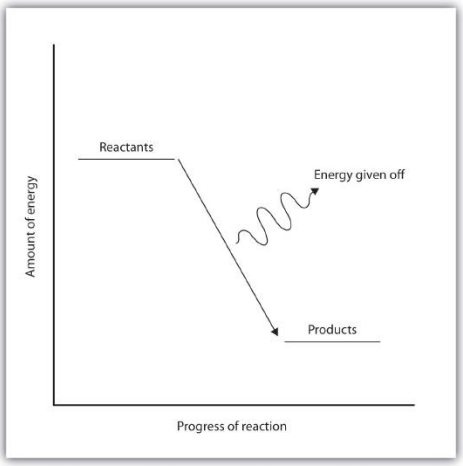


Figure 7.3.2*B*: Exothermic Reactions

Table 7.3.1: 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.
ΔH_{rxn} is positive	ΔH_{rxn} is negative

Endothermic Reactions	Exothermic Reactions
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.

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7.4: Why Do Chemical Reactions Occur? Free Energy

Learning Outcomes

- Describe the meaning of a spontaneous reaction in terms of enthalpy and entropy changes.
- Define free energy.
- Determine the spontaneity of a reaction based on the value of its change in free energy at high and low temperatures.

Spontaneous Reactions

A **spontaneous reaction** *is a reaction that favors the formation of products at the conditions under which the reaction is occurring*. A roaring bonfire (see Figure 7.4.1 below) is an example of a spontaneous reaction. A fire is *exothermic*, which means a decrease in the energy of the system as energy is released to the surroundings as heat. The products of a fire are composed mostly of gases such as carbon dioxide and water vapor, so the entropy of the system increases during most combustion reactions. This combination of a decrease in energy and an increase in entropy means that combustion reactions occur spontaneously.



Figure 7.4.1: Combustion reactions, such as this fire, are spontaneous reactions. Once the reaction begins, it continues on its own until one of the reactants (fuel or oxygen) is gone.

A **nonspontaneous reaction** *is a reaction that does not favor the formation of products at the given set of conditions*. In order for a reaction to be nonspontaneous, one or both of the driving forces must favor the reactants over the products. In other words, the reaction is endothermic, is accompanied by a decrease in entropy, or both. Out atmosphere is composed primarily of a mixture of nitrogen and oxygen gases. One could write an equation showing these gases undergoing a chemical reaction to form nitrogen monoxide.

$$\mathrm{N_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{NO}\,(g) \tag{7.4.1}$$

Fortunately, this reaction is nonspontaneous at normal temperatures and pressures, it is a highly endothermic reaction. However, nitrogen monoxide is capable of being produced at very high temperatures, and this reaction has been observed to occur as a result of lightning strikes.

One must be careful not to confuse the term spontaneous with the notion that a reaction occurs rapidly. A spontaneous reaction is one in which product formation is favored, even if the reaction is extremely slow. You do not have to worry about a piece of paper on your desk suddenly bursting into flames, although its combustion is a spontaneous reaction. What is missing is the required activation energy to get the reaction started. If the paper were to be heated to a high enough temperature, it would begin to burn, at which point the reaction would proceed spontaneously until completion.

Entropy as a Driving Force

An example of a very simple spontaneous process is that of a melting ice cube. Energy is transferred from the room to the ice cube, causing it to change from the solid to the liquid state.

$$\mathrm{H_2O}\,(s) + 6.01\ \mathrm{kJ} \rightarrow \mathrm{H_2O}\,(l) \tag{7.4.2}$$

The solid state of water, ice, is highly *ordered* because its molecules are fixed in place. The melting process frees the water molecules from their hydrogen-bonded network and allows them a greater degree of movement. Water is more *disordered* than ice. The change from the solid to the liquid state of any substance corresponds to an increase in the disorder of the system.

The tendency in nature for systems to proceed toward a state of greater disorder or randomness is called **entropy**, which is symbolized by *S*, and expressed in units of Joules per mole-kelvin, $\mathrm{J}/(\mathrm{mol}\cdot\mathrm{K})$. Larger values of *S* indicate that the particles in a substance have more disorder or randomness. In the example above, the particles in the ice cube (solid water) have lower freedom of motion, they are less random. As the ice melts to liquid water, the particles become more disordered and entropy increases. If the liquid water was heated further, the particles would even gain more freedom of motion, become more disordered, and eventually change to a gas, which has even higher entropy.

Chemical reactions also tend to proceed in such a way as to increase the total entropy of the system, measured by the **entropy change (ΔS)** between reactants and products. How can you tell if a certain reaction shows an increase or a decrease in entropy? The states of the reactants and produces provide certain clues. The general cases below illustrate entropy at the molecular level.

1. For a given substance, the entropy of the liquid state is greater than the entropy of the solid state. Likewise, the entropy of the gas is greater than the entropy of the liquid. Therefore, entropy increases in processes in which solid or liquid reactants form gaseous products. Entropy also increases when solid reactants form liquid products.
2. Entropy increases when a substance is broken up into multiple parts. The process of dissolving increases entropy because the solute particles become separated from one another when a solution is formed.
3. Entropy increases as temperature increases. An increase in temperature means that the particles of the substance have greater kinetic energy. The faster moving particles have more disorder than particles that are moving more slowly at a lower temperature.
4. Entropy generally increases in reactions in which the total number of product molecules is greater than the total number of reactant molecules. An exception to this rule is when nongaseous products are formed from gaseous reactants.

The examples below will serve to illustrate how the entropy change in a reaction can be predicted.

$$\mathrm{Cl_2}\,(g) \rightarrow \mathrm{Cl_2}\,(l) \tag{7.4.3}$$

The entropy is decreasing because a gas is becoming a liquid.

$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \tag{7.4.4}$$

The entropy is increasing because a gas is being produced, and the number of molecules is increasing.

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g) \tag{7.4.5}$$

The entropy is decreasing because four total reactant molecules are forming two total product molecules. All are gases.

$$\mathrm{AgNO_3}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s) \tag{7.4.6}$$

The entropy is decreasing because a solid is formed from aqueous reactants.

$$\mathrm{H_2}\,(g) + \mathrm{Cl_2}\,(g) \rightarrow 2\mathrm{HCl}\,(g) \tag{7.4.7}$$

The entropy change is unknown (but likely not zero) because there are equal numbers of molecules on both sides of the equation, and all are gases.

Gibbs Free Energy

Many chemical reactions and physical processes release energy that can be used to do other things. When the fuel in a car is burned, some of the released energy is used to power the vehicle. **Free energy** *is energy that is available to do work.* Spontaneous reactions release free energy as they proceed. The determining factors for spontaneity of a reaction depend on both the *enthalpy* and *entropy* changes that occur for the system. The **free energy change (ΔG)** of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{7.4.8}$$

The symbol for free energy is *G*, in honor of American scientist Josiah Gibbs (1839 - 1903), who made many contributions to thermodynamics. The change in Gibbs free energy is equal to the change in enthalpy minus the mathematical product of the change in entropy multiplied by the Kelvin temperature. Each thermodynamic quantity in the equation is for substances in their standard states, as indicated by the $^{\circ}$ superscripts.

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible

combinations. The outcomes for ΔG based on the signs of ΔH and ΔS are outlined in the table below. Recall that $-\Delta \mathrm{H}$ indicates that the reaction is exothermic and a $+\Delta \mathrm{H}$ means the reaction is endothermic. For entropy, $+\Delta \mathrm{S}$ means the entropy is increasing and the system is becoming more disordered. A $-\Delta \mathrm{S}$ means that entropy is decreasing and the system is becoming less disordered (more ordered).

> A process that releases free energy, $(-\Delta G)$, is said to be ***exergonic***. Processes that require free energy $(+\Delta G)$, are ***endergonic***. These terms are used when considering chemical reactions that occur in living systems.

Table 7.4.1: Enthalpy, Entropy, and Free Energy Changes.

ΔH	ΔS	ΔG
negative	positive	always negative
positive	positive	negative at higher temperatures, positive at lower temperatures
negative	negative	negative at lower temperatures, positive at higher temperatures
positive	negative	always positive

Keep in mind that the temperature in the Gibbs free energy equation is the Kelvin temperature, so it can only have a positive value. When ΔH is negative and ΔS is positive, the sign of ΔG will always be negative, and the reaction will be spontaneous at all temperatures. This corresponds to both driving forces being in favor of product formation. When ΔH is positive and ΔS is negative, the sign of ΔG will always be positive, and the reaction can never be spontaneous. This corresponds to both driving forces working against product formation.

When one driving force favors the reaction, but the other does not, it is the temperature that determines the sign of ΔG. Consider first an endothermic reaction (positive ΔH) that also displays an increase in entropy (positive ΔS). It is the entropy term that favors the reaction. Therefore, as the temperature increases, the $T\Delta S$ term in the Gibbs free energy equation will begin to predominate and ΔG will become negative. A common example of a process which falls into this category is the melting of ice (see figure below). At a relatively low temperature (below 273 K), the melting is not spontaneous because the positive ΔH term "outweighs" the $T\Delta S$ term. When the temperature rises above 273 K, the process becomes spontaneous because the larger T value has tipped the sign of ΔG over to being negative.



Figure 7.4.2: Ice melts spontaneously only when the temperature is above 0°C. The increase in entropy is then able to drive the unfavorable endothermic process.

When the reaction is exothermic (negative ΔH) but undergoes a decrease in entropy (negative ΔS), it is the enthalpy term which favors the reaction. In this case, a spontaneous reaction is dependent upon the $T\Delta S$ term being small relative to the ΔH term, so that ΔG is negative. The freezing of water is an example of this type of process. It is spontaneous only at a relatively low temperature. Above $273.$ K, the larger $T\Delta S$ value causes the sign of ΔG to be positive, and freezing does not occur.

Contributors and Attributions

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7.5: How Do Chemical Reactions Occur? Reaction Rates

Learning Outcomes

- Define reaction rate.
- Explain the concept of activation energy.
- Label a diagram with reactants, products, enthalpy of forward and reverse reactions, activation energy of forward and reverse reactions, and activated complex.

Chemical kinetics is the study of the rates of chemical reactions. In this lesson, you will learn how to express the rate of a chemical reaction and about various factors that influence reaction rates.

Expressing Reaction Rate

Chemical reactions vary widely in the speeds with which they occur. Some reactions occur very quickly. It a lighted match is brought into contact with lighter fluid or another flammable liquid, it erupts into flame 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 seconds (s) to run a 100 meter (\left(m \right)\) dash, his rate or speed is given by the distance traveled divided by the time (see figure below).

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100\ \text{m}}{11.0\ \text{s}} = 9.09\ \text{m/s} \tag{7.5.1}$$

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 the be greater than $9.09\ \text{m/s}$ so that taken over the entire race, the average ends up at $9.09\ \text{m/s}$

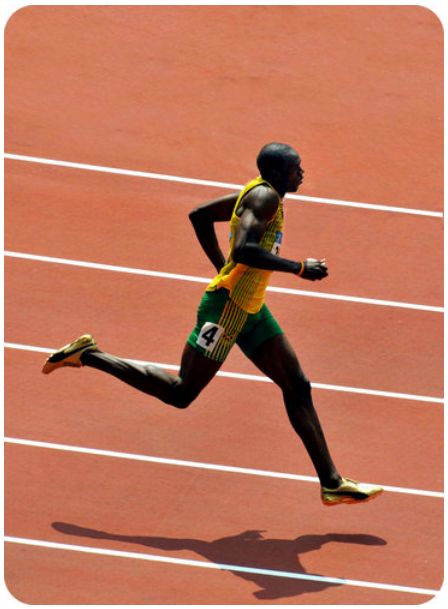


Figure 7.5.1: Usain Bolt set the world record for the 100 meter dash in 2009 with a time of 9.58 seconds. His average running rate over the course of this race was $10.4\ \text{m/s}$, or 23.4 mph.

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 molar (M) aqueous solution of substance A was converted to substance B.

$$\text{A}\,(aq) \rightarrow \text{B}\,(aq) \tag{7.5.2}$$

Suppose that after 20.0 seconds, the concentration of A had dropped from 1.00 M to 0.72 M as it was being converted to substance B. We can express the rate of this reaction as the change in concentration of A divided by the time.

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{[\text{A}]_{\text{final}} - [\text{A}]_{\text{initial}}}{\Delta t} \tag{7.5.3}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of A is its final concentration minus its initial concentration. Because the concentration of 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 M/s.

$$\text{rate} = -\frac{0.72\ \text{M} - 1.00\ \text{M}}{20.0\ \text{s}} = -\frac{-0.28\ \text{M}}{20.0\ \text{s}} = 0.041\ \text{M/s} \tag{7.5.4}$$

Over the first 20.0 seconds of this reaction, the molarity of A decreases by an average rate of 0.041 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).

Collision Theory

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 produce. The first collision is called an ineffective collision, while the second collision is called an effective collision.

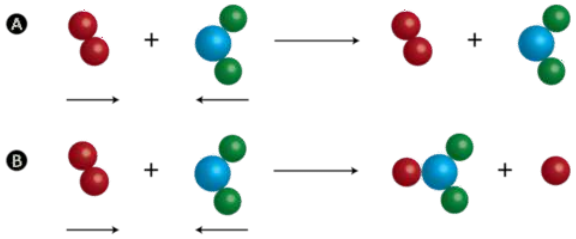


Figure 7.5.2: (A) An ineffective collision is one that does not result in product formation. (B) An effective collision is one in which chemical bonds are broken, and a product is formed.

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 (ΔH) 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.

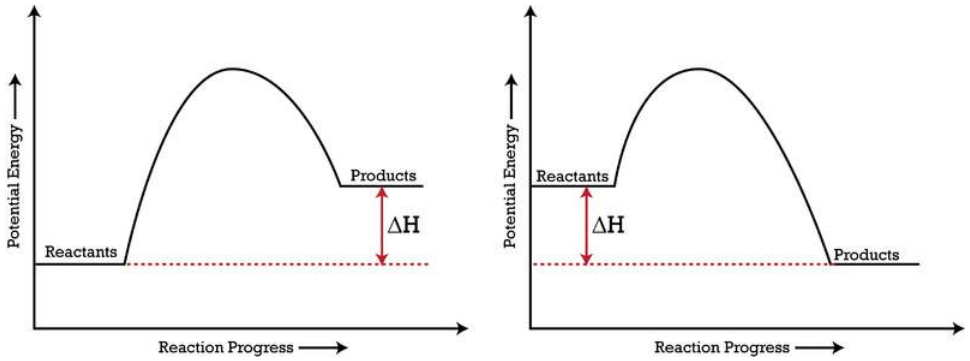


Figure 7.5.3: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (Left) In an endothermic reaction, the energy of the products is greater than the energy of the reactants, and ΔH is positive. (Right) In an exothermic reaction, the energy of the products is lower than the energy of the reactants, and ΔH 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).

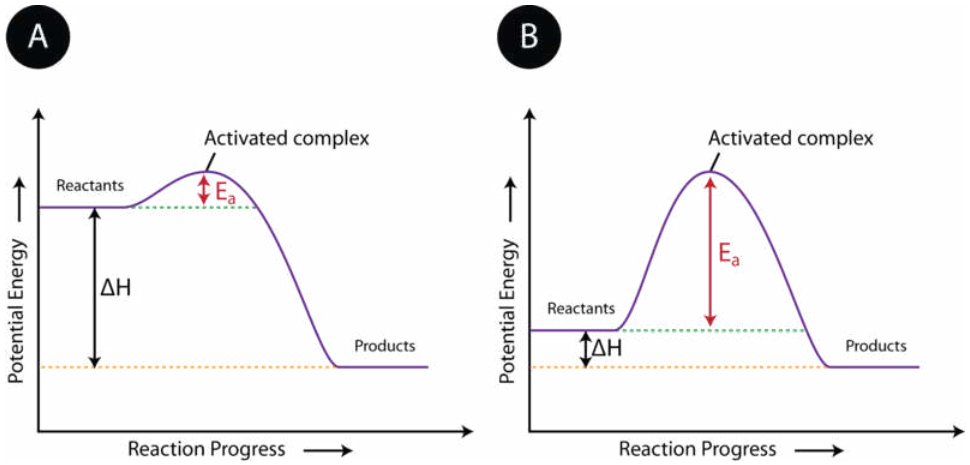


Figure 7.5.4: The activation energy (E_a) of a reaction is the barrier that must be overcome in order for the reactants to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow.

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.

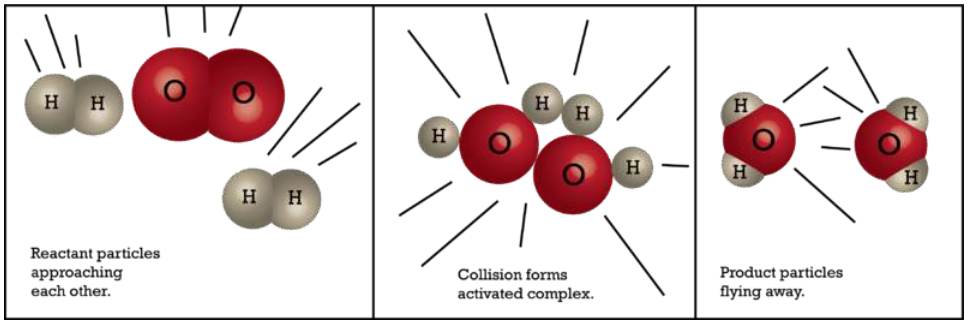


Figure 7.5.5: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve.

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7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

Learning Outcomes

- Describe how temperatures, concentration of reactant, and a catalyst affect the reaction rate.

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.

Concentration

Increasing the concentration of one or more of the reacting substances generally increases the reaction rate. When more particles are present in a given amount of space, a greater number of collisions will naturally occur between those particles. Since the rate of a reaction is dependent on the frequency of collisions between the reactants, the rate increases as the concentration increases.

Temperature

Raising the temperature of a chemical reaction results in a higher reaction rate. When the reactant particles are heated, they move faster and faster, resulting in a greater frequency of collisions. An even more important effect of the temperature increase is that the collisions occur with a greater force, which means the reactants are more likely to surmount the activation energy barrier and go on to form products. Increasing the temperature of a reaction increases not only the frequency of collisions, but also the percentage of those collisions that are effective, resulting in an increased reaction rate.

Paper is certainly a highly combustible material, but paper does not burn at room temperature because the activation energy for the reaction is too high. The vast majority of collisions between oxygen molecules and the paper are ineffective. However, when the paper is heated by the flame from a match, it reaches a point where the molecules now have enough energy to react. The reaction is very exothermic, so the heat released by the initial reaction will provide enough energy to allow the reaction to continue, even if the match is removed. The paper continues to burn rapidly until it is gone.

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.

$$2\mathrm{H_2O_2}\,(aq) \overset{\mathrm{MnO_2}}{\rightarrow} 2\mathrm{H_2O}\,(l) + \mathrm{O_2}\,(g) \tag{7.6.1}$$

A catalyst works by changing the mechanism of the reaction, which can be though 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.

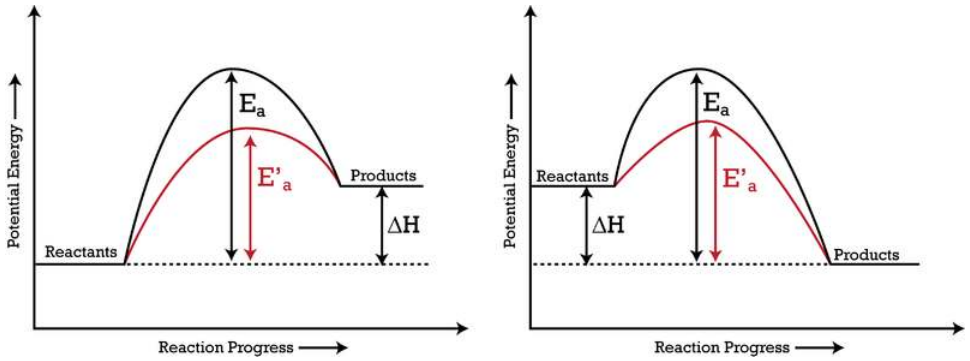


Figure 7.6.7: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by E_a, while the catalyzed reaction is shown by E_a'. The heat of reaction (ΔH) is unchanged by the presence of the catalyst.

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.

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7.7: Reversible Reactions and Chemical Equilibrium

Learning Objectives

- Define chemical equilibrium.
- Recognize chemical equilibrium as a dynamic process.

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 because it is a **reversible reaction**, meaning it can go in either direction. As soon as there is enough product formed, the HI can react and the reverse chemical reaction occurs essentially "undoing" the first reaction:

$$2HI \rightarrow H_2 + I_2$$

Eventually, the reverse reaction proceeds so quickly that it matches the speed of the forward reaction. When that happens, the concentration of the reactants and products remains constant, there is no further change; the reaction has reached **chemical equilibrium** (sometimes just spoken as *equilibrium*; plural *equilibria*), the point at which the forward and reverse processes balance each other's progress.

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.

Example 7.7.1

Write the equilibrium equation that exists between calcium carbonate as a reactant and calcium oxide and carbon dioxide as products.

Solution

As this is an equilibrium situation, a double arrow is used. The equilibrium equation is written as follows:

$$CaCO_3 + \rightleftharpoons CaO + CO_2$$

Exercise 7.7.1

Write the equilibrium equation between elemental hydrogen and elemental oxygen as reactants and water as the product.

Answer

$$2H_2 + O_2 + \rightleftharpoons 2H_2O$$

One thing to note about equilibrium is that the reactions do not stop; both the forward reaction and the reverse reaction continue to occur. They both occur at the same rate, so any overall change by one reaction is canceled by the reverse reaction. We say that chemical equilibrium is *dynamic*, rather than static. Also, because both reactions are occurring simultaneously, the equilibrium can be written backward. For example, representing an equilibrium as

$$H_2 + I_2 \rightleftharpoons 2HI$$

is the same thing as representing the same equilibrium as

$$2HI \rightleftharpoons H_2 + I_2$$

The reaction must be at equilibrium for this to be the case, however.

Key Takeaways

- Chemical reactions eventually reach equilibrium, a point at which forward and reverse reactions balance each other's progress.
- Chemical equilibria are dynamic: the chemical reactions are always occurring; they just cancel each other's progress.

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7.8: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria

Learning Objectives

- Define *Le Chatelier's principle*.
- Predict the direction of shift for an equilibrium under stress.

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called **Le Chatelier's principle**: If an equilibrium is stressed, then the reaction shifts to reduce the stress.

Effect of Changes in Concentration

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

Example 7.8.1

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In which direction—toward reactants or toward products-—does the reaction shift 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 toward products to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

Exercise 7.8.1

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answers

1. toward reactants
2. toward reactants

It is worth noting that when reactants or products are added or removed, *the value of the* K_{eq} *does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

Effect of Changes in Pressure and Temperature

How does an equilibrium react to a change in *pressure*? Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

Example 7.8.2

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 toward the products side.

Exercise 7.8.2

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

Answer

Reaction shifts toward reactants.

What is the effect of *temperature* changes on an equilibrium? It depends on whether the reaction is endothermic or exothermic. Recall that *endothermic* means that energy is absorbed by a chemical reaction, while *exothermic* means that energy is given off by the reaction. As such, energy can be thought of as a reactant or a product, respectively, of a reaction:

endothermic reaction: energy + reactants → products

exothermic reaction: reactants → products + energy

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for exothermic reactions), and the equilibrium shifts accordingly.

Example 7.8.3

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 back toward reactants.

Exercise 7.8.3

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

Answer

Equilibrium shifts toward reactants.

In the case of temperature, the value of the equilibrium has changed because the K_{eq} is dependent on temperature. That is why equilibria shift with changes in temperature.

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds. However, a catalyst does not affect the extent or position of a reaction at equilibrium. It helps a reaction achieve equilibrium faster.

Chemistry is Everywhere: Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?



Figure 7.8.1 Garden Equilibria © Thinkstock. This species of hydrangea has flowers that can be either red or blue. Why the color difference?

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H^+ or OH^- ions that affect the color of the flowers. Rather, it is the presence of aluminum that causes the color change.

The solubility of aluminum in soil, and the ability of plants to absorb it, is dependent upon the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue, as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

Key Takeaways

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- The direction of shift can be predicted for changes in concentrations, temperature, or pressure.
- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

Exercise 7.8.1

1. Define *Le Chatelier's principle*.
2. What is meant by a stress? What are some of the ways an equilibrium can be stressed?
3. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + I_2(s) + 53kJ \rightleftharpoons 2HI(g)$$

a. decreased temperature
b. increased pressure
c. removal of HI

4. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g) + 546kJ$$

a. increased temperature
b. addition of H_2
c. decreased pressure

5. Given this equilibrium, predict the direction of shift for each stress.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 196kJ$$

a. removal of SO_3
b. addition of O_2
c. decreased temperature

6. Given this equilibrium, predict the direction of shift for each stress.

$$CO_2(g) + C(s) + 171kJ \rightleftharpoons 2CO(g)$$

a. addition of CO
b. increased pressure
c. addition of a catalyst

7. The synthesis of NH_3 uses this chemical reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92kJ$$

Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH_3.

8. The synthesis of $CaCO_3$ uses this chemical reaction.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + 180kJ$$

Identify three stresses that can be imposed on the equilibrium to maximize the amount of $CaCO_3$.

Answers

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.
2.
3. a. toward reactants

- toward reactants
- toward products
-
- a. toward products
  b. toward products
  c. toward products
-
- increased pressure, decreased temperature, removal of NH_3

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CHAPTER OVERVIEW

8: Gases, Liquids, and Solids

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8.14: Changes of State Calculations

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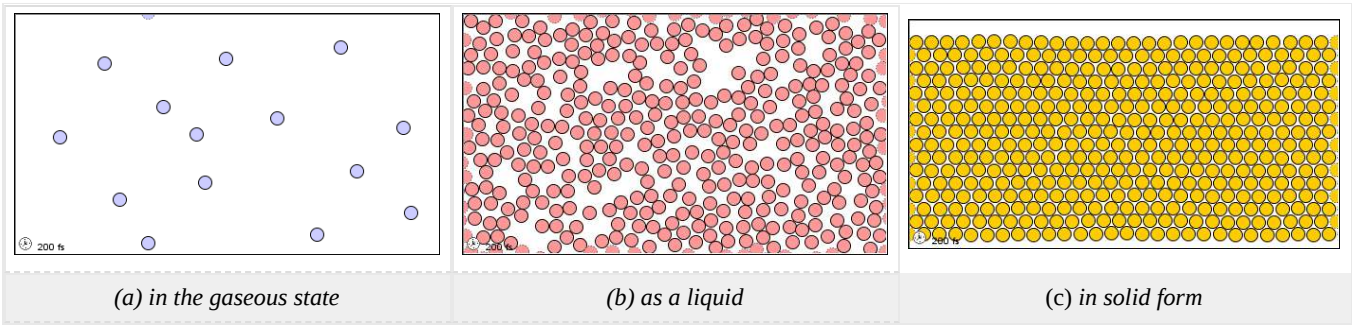
8.1: States of Matter and Their Changes

Learning Objectives

- Review the states of matter and their properties
- Describe how change in temperature will affect the state of matter.

Previously, you were introduced to the three states, also called phases, of matter; solid, liquid, and gas. A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid*** *phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid*** *phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas*** *phase*, in which individual particles are separated from each other by relatively large distances (see Figure 8.1.1).

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



(a) in the gaseous state | *(b) as a liquid* | (c) *in solid form*

Figure 8.1.1: Molecular level picture of gases, liquids and solids.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These **changes of state** are often called phase changes. The six most common phase changes are shown in Figure 8.1.2.

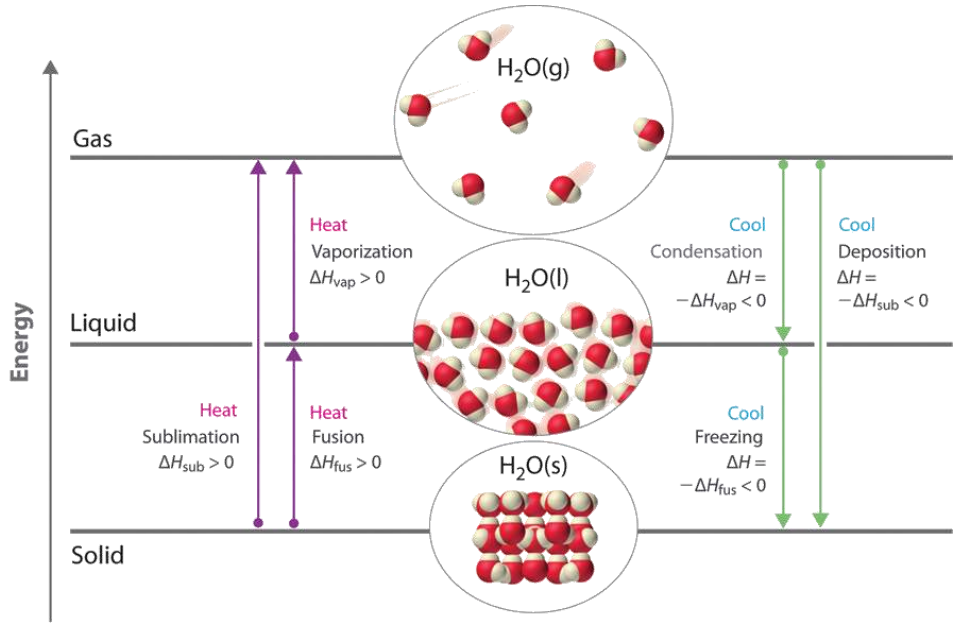


Figure 8.1.2: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the enthalpy, ΔH, 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; the ΔH is positive (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; the ΔH is negative (exothermic). The energy change associated with each common phase change is shown in Figure 8.1.2.

> *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 molar **enthalpy of fusion** (ΔH_{fus}), is the energy required to convert a solid to a liquid, a process known as fusion (or melting). As noted above, the process of melting requires energy and therefore, the (ΔH_{fus}) is positive. The reverse process of freezing would release energy making the (ΔH_{fus}) negative. The molar **enthalpy of vaporization** (ΔH_{vap}), is the energy required to convert a liquid to a gas, known as vaporization. Melting points, enthalpies of fusion, boiling points, and enthalpies of vaporization for selected compounds are listed in Table 8.1.1.

Table 8.1.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
$CH_3(CH_2)_4CH_3$ (*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).

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8.2: Intermolecular Forces

Learning Objective

- Identify the different types of intermolecular forces.
- Relate the physical properties of a substance to the strength of attractive forces.

Why does a substance exist as a solid, liquid, or a gas at specific temperatures? Why do some substances evaporate quickly or melt more easily? These questions can be answered by considering the balance between the energy of the particles and **intermolecular forces** (or intermolecular interactions) between the particles. If the forces between particles are strong enough, the substance is a liquid or, if stronger, a solid. If the forces between particles are weak and sufficient energy is present, the particles separate from each other, so the gas phase is the preferred phase. The energy of the particles is mostly determined by temperature, so temperature is the main variable that determines what phase is stable at any given point.

There are three types of intermolecular forces: *London Dispersion, dipole-dipole, and hydrogen bonding*, collectively termed van der Waals forces, that will be introduced below.

London Dispersion Forces

There are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge (a temporary dipole moment) that disappears almost as soon as it appears. These very weak intermolecular interactions are called **dispersion forces** (or **London dispersion forces**, named for the physicist Fritz London, who first described this force in the early 1900s).

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. **Larger and heavier atoms and molecules** exhibit **stronger dispersion forces** than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 8.2.1.

Table 8.2.1: **Melting and Boiling Points of the Halogens**

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 8.2.1

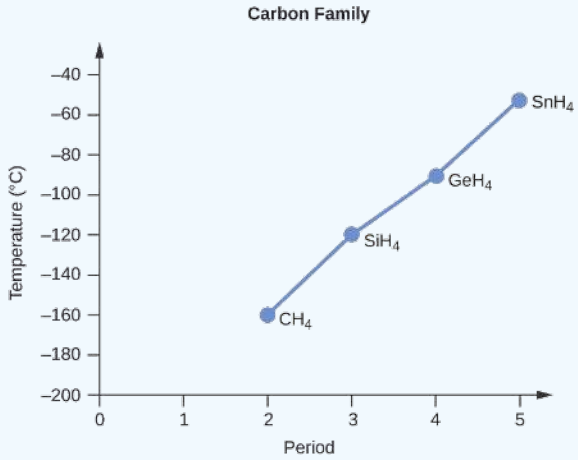
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$CH_4 < SiH_4 < GeH_4 < SnH_4$

A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



Exercise 8.2.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

Dipole-Dipole Intermolecular Forces

Recall that a polar molecule will have a net unequal distribution of electrons in its covalent bonds resulting in a partial positive charge on one side of the molecule and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole***. The electrostatic attraction between oppositely charged ends of polar molecules are called **dipole-dipole interactions**, (as illustrated in Figure 8.2.1). Dipole-dipole attractions are between permanent dipoles and are therefore generally *stronger* than dispersion forces, which are between temporary dipoles. Thus, a polar molecule such as CH_2Cl_2 has a significantly higher boiling point (313 K, or 40°C) than a nonpolar molecule like CF_4 (145 K, or −128°C), even though it has a lower molar mass (85 g/mol vs. 88 g/mol).

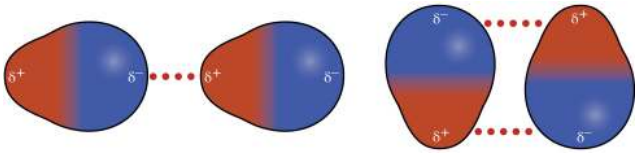


Figure 8.2.1: This image illustrates a dipole-dipole interaction, two arrangements of polar molecules that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

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Example 8.2.2

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

Exercise 8.2.2

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonds

An unusually strong form of dipole-dipole interaction is called **hydrogen bonding**. Hydrogen bonding is found in molecules with an H atom bonded to an N atom, an O atom, or an F atom. Such covalent bonds are very polar, and the dipole-dipole interaction between these bonds in two or more molecules is strong enough to create a new category of intermolecular force. Hydrogen bonding is the reason water has unusual properties. For such a small molecule (its molar mass is only 18 g/mol), H_2O has relatively high melting and boiling points. Its boiling point is 373 K (100°C), while the boiling point of a similar molecule, H_2S, is 233 K (−60°C). This is because H_2O molecules experience hydrogen bonding, while H_2S molecules do not. This strong attraction between H_2O molecules requires additional energy to separate the molecules in the condensed phase, so its boiling point is higher than would be expected. Hydrogen bonding is also responsible for water's ability as a solvent, its high heat capacity, and its ability to expand when freezing; the molecules line up in such a way that there is extra space between the molecules, increasing its volume in the solid state (Figure 8.2.2).

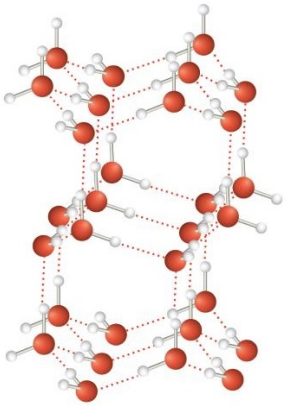


Figure 8.2.2: Hydrogen Bonding. When water solidifies, hydrogen bonding between the molecules forces the molecules to line up in a way that creates empty space between the molecules, increasing the overall volume of the solid. This is why ice is less dense than liquid water.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 8.2.3.

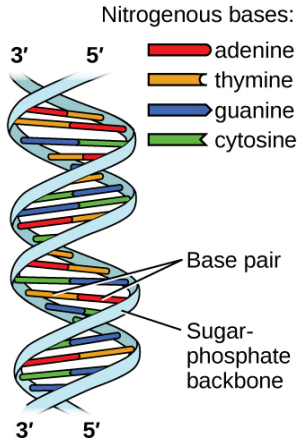


Figure 8.2.3: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 8.2.4

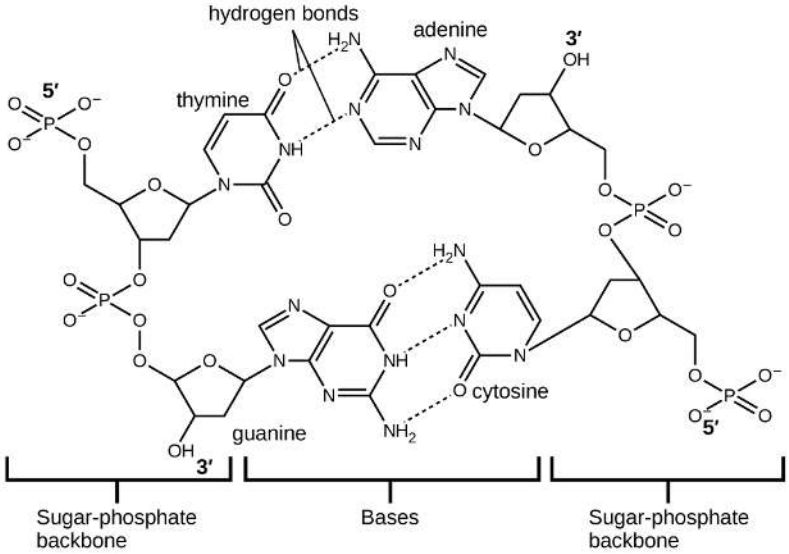


Figure 8.2.4: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

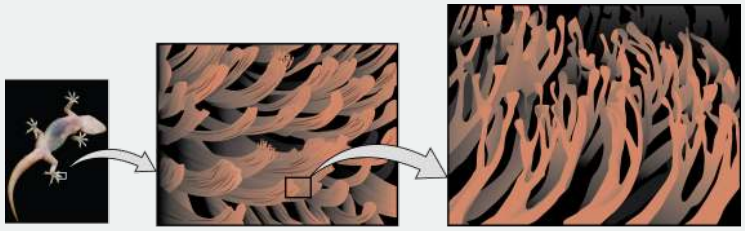


Figure 8.2.12: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)*

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.1.12, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar Cl_2 has a higher boiling point than polar HCl.

Table 8.2.3: Intermolecular Forces and Boiling Points

Substance	Strongest Intermolecular Force	Boiling Point (°C)
H_2	dispersion	-253
Ne	dispersion	-246
O_2	dispersion	-183
Cl_2	dispersion	-34
HCl	dipole-dipole	-85
HBr	dipole-dipole	-66
H_2S	dipole-dipole	-61

Substance	Strongest Intermolecular Force	Boiling Point (°C)
NH_3	hydrogen bonding	-33
HF	hydrogen bonding	20
H_2O	hydrogen bonding	100

Example 8.2.3

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 8.2.3

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Example 8.2.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

? Exercise 8.2.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH_3NH_2)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

Answer

a. dipole-dipole, hydrogen bonding

b. ionic forces (solid at room temperature)

c. dipole-dipole

Concept Review Exercise

1. What types of intermolecular interactions can exist in compounds?

2. What is the difference between covalent network and covalent molecular compounds?

Answer

1. ionic bonding, network covalent, dispersion forces, dipole-dipole interactions, and hydrogen bonding.

2. Covalent network compounds contain atoms that are covalently bonded to other individual atoms in a giant 3-dimensional network. Covalent molecular compounds contain individual molecules that are attracted to one another through dispersion, dipole-dipole or hydrogen bonding.

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: dipole-dipole interactions, hydrogen bonding, and dispersion forces.
- Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another.
- Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.
- The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size.

Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.

2. List the three common phases in the order they exist from lowest energy to highest energy.

3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.

4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.

5. What type of intermolecular interaction is predominate in each substance?

   a. water (H_2O)
   b. sodium sulfate (Na_2SO_4)
   c. decane ($C_{10}H_{22}$)

6. What type of intermolecular interaction is predominate in each substance?

   a. diamond (C, crystal)
   b. helium (He)
   c. ammonia (NH_3)

7. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.
8. Sulfur dioxide (SO_2) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO_2 molecule?
9. What are some of the physical properties of substances that experience covalent network bonding?
10. What are some of the physical properties of substances that experience only dispersion forces?

Answers

1. solid, liquid, and gas

2. solid, liquid, and gas

3. London forces, hydrogen bonding, and ionic interactions

4. dispersion, dipole-dipole, network covalent

5. a. hydrogen bonding
   b. ionic interactions
   c. dispersion forces

6. a. network covalent
b. dispersion
c. hydrogen bonding

7. The two covalent bonds are oriented in such a way that their dipoles cancel out.

8. SO_2 is not a linear molecule. It has a bent or V-shape.

9. very hard, high melting point

10. very soft, very low melting point

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8.3: Gases and the Kinetic-Molecular Theory

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**. The kinetic theory of gases is based on the following statements:

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 8.3.1 shows a representation of how we mentally picture the gas phase.

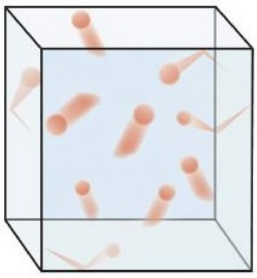


Figure 8.3.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion, with a lot of distance between the particles.

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, and 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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8.4: Gas Pressure

Learning Objectives

- To describe and measure the pressure of a gas.

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8.5: Boyle's Law - The Relation between Volume and Pressure

Learning Objectives

- Define the relationship between gas volume and pressure, Boyle's Law.
- Use Boyle's Law to calculate changes in pressure or volume of a gas.

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. We say 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 (*k*) for a given amount of gas at a constant temperature:

$$P \times V = k \ (at\ constant\ n\ and\ T)$$

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

$$P_1V_1 = k = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \ (at\ constant\ n\ and\ T)$$

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 8.5.1 shows two representations of how Boyle's law works.

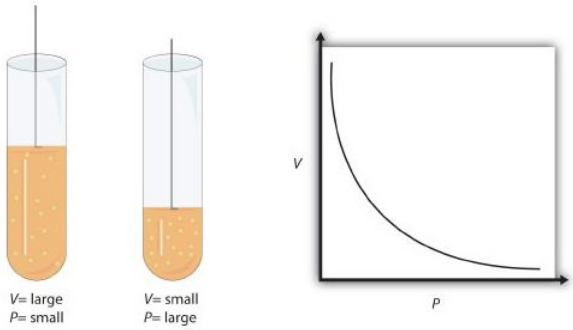


Figure 8.5.1: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

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 8.5.1

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

First, determine what quantities we are given. We are given an initial pressure and an initial volume, so let these values be P_1 and V_1:

$$P_1 = 2.44 \text{ atm and } V_1 = 4.01 \text{ L}$$

We are given another quantity, final pressure of 1.93 atm, but not a final volume. This final volume is the variable we will solve for.

$$P_2 = 1.93 \text{ atm and } V_2 = ? \text{ L}$$

Substituting these values into Boyle's law, we get

$$(2.44 \text{ atm})(4.01 \text{ L}) = (1.93 \text{ atm})V_2$$

To solve for the unknown variable, we isolate it by dividing both sides of the equation by 1.93 atm—both the number *and* the unit:

$$\frac{(2.44\,atm)(4.01\,L)}{1.93\,atm} = \frac{(1.93\,atm)\,V_2}{1.93\,atm}$$

Note that, on the left side of the equation, the unit *atm* is in the numerator and the denominator of the fraction. They cancel algebraically, just as a number would. On the right side, the unit *atm* and the number 1.93 are in the numerator and the denominator, so the entire quantity cancels:

$$\frac{(2.44\ \cancel{atm})(4.01\,L)}{1.93\ \cancel{atm}} = \frac{(1.93\ \cancel{atm})\,V_2}{1.93\ \cancel{atm}}$$

What we have left is

$$\frac{(2.44)(4.01\,L)}{1.93} = V_2$$

Now we simply multiply and divide the numbers together and combine the answer with the L unit, which is a unit of volume. Doing so, we get $V_2 = 5.07\,L$

Does this answer make sense? 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 8.5.1

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 or volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

Example 8.5.2

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

We can still use Boyle's law to answer this, but now the two volume quantities have different units. It does not matter which unit we change, as long as we perform the conversion correctly. Let us change the 0.663 L to milliliters:

$$0.663\ L \times \frac{1000\ ml}{1\ L} = 663\ ml$$

Now that both volume quantities have the same units, we can substitute into Boyle's law:

$$(722\ torr)(88.8\ ml) = P_2(663\ ml)$$

$$\frac{(722\ torr)(88.8)\ ml}{(663\ ml)} = P_2$$

The mL units cancel, and we multiply and divide the numbers to get P_2 = 96.7 torr

The volume is increasing, and the pressure is decreasing, which is as expected for Boyle's law.

? Exercise 8.5.2

If V_1 = 456 mL, P_1 = 308 torr, and P_2 = 1.55 atm, what is V_2?

Answer

119 mL

To Your Health: Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure 8.5.2).

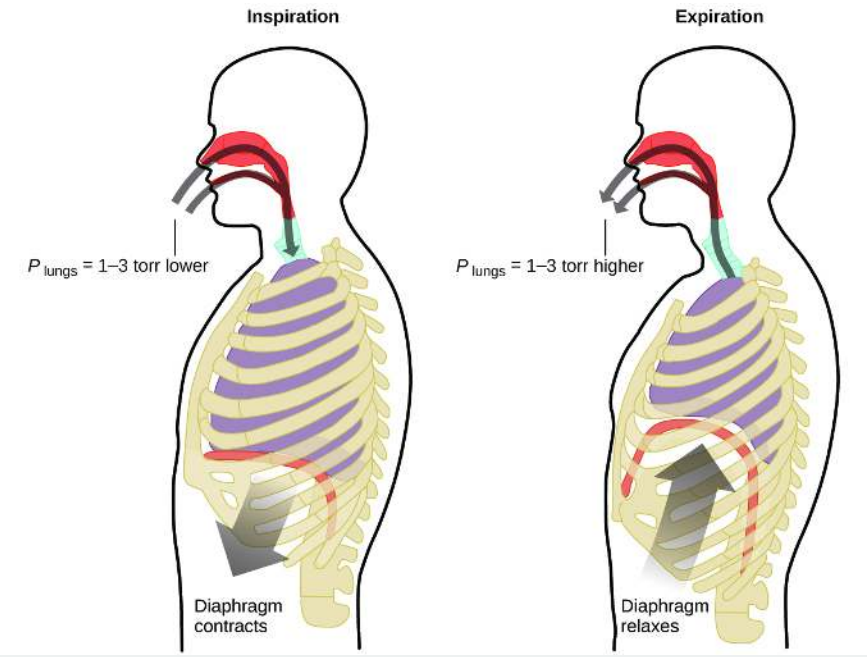


Figure 8.5.2: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

This figure contains two diagrams of a cross section of the human head and torso. The first diagram on the left is labeled “Inspiration.” It shows curved arrows in gray proceeding through the nasal passages and mouth to the lungs. An arrow points downward from the diaphragm, which is relatively flat, just beneath the lungs. This arrow is labeled “Diaphragm contracts.” At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr lower” is provided. The second, similar diagram, which is labeled “Expiration,” reverses the direction of both arrows. Arrows extend from the lungs out through the nasal passages and mouth. Similarly, an arrow points up to the diaphragm, showing a curved diaphragm and lungs reduced in size from the previous image. This arrow is labeled “Diaphragm relaxes.” At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr higher” is provided.

Summary

- The behavior of gases can be modeled with gas laws.
- Boyle's law relates a gas's pressure and volume at constant temperature and amount.

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8.6: Charles's Law- The Relation between Volume and Temperature

Learning Objectives

- Define the relationship between gas temperature and volume, Charles's Law.
- Use Charles's Law to calculate changes in temperature or volume of a gas.

In addition to pressure and volume, another measurable characteristics of a gas is temperature (*T*). Perhaps one can vary the temperature of a gas sample and note what effect it has on the other properties of the gas. Early scientists did just this, discovering that if the amount of a gas and its pressure are kept constant, then changing the temperature changes the volume (*V*). As temperature increases, volume increases; as temperature decreases, volume decreases. We say that these two characteristics are *directly related*.

Kelvin Temperature Scale

A mathematical relationship between *V* and *T* should be possible except for one thought: what temperature scale should we use? We know from previous chapters that scientists uses several possible temperature scales. Experiments show that the volume of a gas is related to its absolute temperature in **Kelvin**, *not its temperature in degrees Celsius*. If the temperature of a gas is expressed in Kelvins, then experiments show that the *ratio* of volume to temperature is a constant (*k*):

$$\frac{V}{T} = k$$

Charles's Law

We can modify this equation as we modified Boyle's law: the initial conditions V_1 and T_1 have a certain value, and the value must be the same when the conditions of the gas are changed to some new conditions V_2 and T_2, as long as pressure and the amount of the gas remain constant. Thus, we have another gas law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \; (at \; constant \; P \; and \; n)$$

This gas law is commonly referred to as **Charles's law**, after the French scientist Jacques Charles, who performed experiments on gases in the 1780s. The tactics for using this mathematical formula are similar to those for Boyle's law. To determine an unknown quantity, use algebra to isolate the unknown variable by itself and in the numerator; the units of similar variables must be the same. But we add one more tactic: all temperatures must be expressed in the absolute temperature scale (Kelvin). As a reminder, we review the conversion between the absolute temperature scale and the Celsius temperature scale:

$$\text{K} = ^\circ\text{C} + 273$$

where K represents the temperature in kelvins, and °C represents the temperature in degrees Celsius.

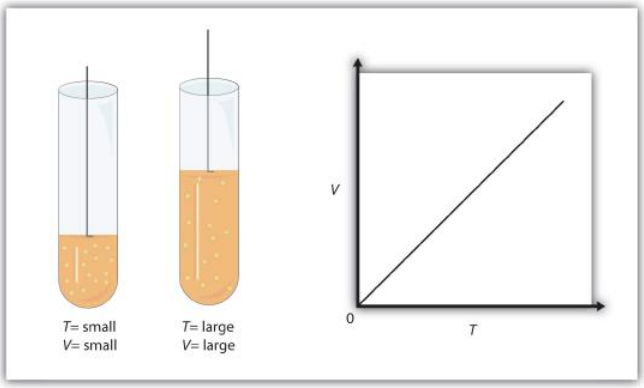


Figure 8.6.1: Charles's Law. A piston having a certain volume and temperature (left piston) will have twice the volume when its temperature is twice as much (right piston). One can also plot V versus T for a given amount of gas at a certain pressure; such a plot will look like the graph on the right.

Example 8.6.1

A sample of gas has an initial volume of 34.8 mL and an initial temperature of 315 K. What is the new volume if the temperature is increased to 559 K? Assume constant pressure and amount for the gas.

Solution

First, we assign the given values to their variables. The initial volume is V_1, so V_1 = 34.8 mL, and the initial temperature is T_1, so T_1 = 315 K. The temperature is increased to 559 K, so the final temperature T_2 = 559 K. We note that the temperatures are already given in kelvins, so we do not need to convert the temperatures. Substituting into the expression for Charles's law yields

$$\frac{34.8\,ml}{315\,K} = \frac{V_2}{559\,K}$$

We solve for V_2 by algebraically isolating the V_2 variable on one side of the equation. We do this by multiplying both sides of the equation by 559 K (number and unit). When we do this, the temperature unit cancels on the left side, while the entire 559 K cancels on the right side:

$$\frac{(559\ \cancel{K})(34.8\,ml)}{315\ \cancel{K}} = \frac{V_2(\ 559\ \cancel{K})}{559\ \cancel{K}}$$

The expression simplifies to

$$\frac{(559)(34.8\,ml)}{315} = V_2$$

By multiplying and dividing the numbers, we see that the only remaining unit is mL, so our final answer is

V_2 = 61.8 mL

Does this answer make sense? We know that as temperature increases, volume increases. Here, the temperature is increasing from 315 K to 559 K, so the volume should also increase, which it does.

Exercise 8.6.1

If V_1 = 3.77 L and T_1 = 255 K, what is V_2 if T_2 = 123 K?

Answer

1.82 L

It is more mathematically complicated if a final temperature must be calculated because the *T* variable is in the denominator of Charles's law. There are several mathematical ways to work this, but perhaps the simplest way is to take the reciprocal of Charles's law. That is, rather than write it as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

write the equation as

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

It is still an equality and a correct form of Charles's law, but now the temperature variable is in the numerator, and the algebra required to predict a final temperature is simpler.

Example 8.6.2

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must the temperature of the gas be for its volume to be 25.0 L?

Solution

Here, we are looking for a final temperature, so we will use the reciprocal form of Charles's law. However, the initial temperature is given in degrees Celsius, not kelvins. We must convert the initial temperature to kelvins:

−67°C + 273 = 206 K

In using the gas law, we must use T_1 = 206 K as the temperature. Substituting into the reciprocal form of Charles's law, we get

$$\frac{206\ K}{34.8\ L} = \frac{T_2}{25.0\ L}$$

Bringing the 25.0 L quantity over to the other side of the equation, we get

$$\frac{(25.0\ \cancel{L})(206\ K)}{34.8\ \cancel{L}} = T_2$$

The L units cancel, so our final answer is T_2 = 148 K

This is also equal to −125°C. As temperature decreases, volume decreases, which it does in this example.

? Exercise 8.6.2

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 a gas's volume and temperature at constant pressure and amount.
- In gas laws, temperatures must always be expressed in kelvins.

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8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature

Learning Objectives

- Define the relationship between gas pressure and temperature, Gay-Lussac's Law.

A third gas law may be derived as a corollary to Boyle's and Charles's laws. Suppose we double the thermodynamic temperature of a sample of gas. According to Charles's law, the volume should double. Now, how much pressure would be required at the higher temperature to return the gas to its original volume? According to Boyle's law, we would have to double the pressure to halve the volume. Thus, if the volume of gas is to remain the same, doubling the temperature will require doubling the pressure. This law was first stated by the Frenchman Joseph Gay-Lussac (1778 to 1850). According to **Gay-Lussac's law**, *for a given amount of gas held at constant volume, the pressure is proportional to the absolute temperature.* Mathematically,

$$P \propto T \text{ or } P = k \times T \text{ or } \frac{P}{T} = k$$

where $\propto$ means "is proportional to," and *k* is a proportionality constant that depends on the identity, amount, and volume of the gas. In terms of two sets of data: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called absolute zero). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Gay-Lussac's law tells us that it may be dangerous to heat a gas in a closed container. The increased pressure might cause the container to explode, as you can see in the video below. The video shows very, very cold nitrogen gas in a bottle being warmed by the air. Since the bottle's volume is relatively constant, as the temperature of the nitrogen gas (formed when the liquid nitrogen boils) increases, so does the pressure inside the bottle until, finally, BOOM!



Example 8.7.1: Temperature

A container is designed to hold a pressure of 2.5 atm. The volume of the container is 20.0 cm^3, and it is filled with air at room temperature (20°C) and normal atmospheric pressure. Would it be safe to throw the container into a fire where temperatures of 600°C would be reached?

Solution

Using the common-sense method, we realize that the pressure will increase at the higher temperature, and so:

$$P_2 = 1.0 \text{ atm} \times \frac{(273.15 + 600)\text{ K}}{(273.15 + 20)\text{ K}} = 3.0 \text{ atm}$$

This would exceed the safe strength of the container. Note that the volume of the container was not needed to solve the problem.

This concept works in reverse, as well. For instance, if we subject a gas to lower temperatures than their initial state, the external atmosphere can actually force the container to shrink. The following video demonstrates how a sample of hot gas, when cooled will collapse a container. A syringe barrel is filled with hot steam (vaporized water) and a plunger placed to cap off the end. The syringe is then placed in a beaker of ice water to cool the internal gas. When the temperature of the water vapor decreases, the pressure exerted by the vapor decreases as well. This leads to a difference in pressure between the vapor inside the barrel and the atmosphere. Atmospheric pressure then pushes the plunger into the barrel.

Summary

- Gay-Lussac's law relates a gas's temperature and pressure at constant volume and amount.
- In gas laws, temperatures must always be expressed in kelvins.

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8.8: The Combined Gas Law

Learning Objectives

- Use the combined gas law to determine the relationships between pressure, volume, and temperature of a gas.

One thing we notice about all gas laws, collectively, is that volume and pressure are always in the numerator, and temperature is always in the denominator. This suggests that we can propose a gas law that combines pressure, volume, and temperature. This gas law is known as the **combined gas law**, and its mathematical form is:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \; at \; constant \; n$$

This allows us to follow changes in all three major properties of a gas. Again, the usual warnings apply about how to solve for an unknown algebraically (isolate it on one side of the equation in the numerator), units (they must be the same for the two similar variables of each type), and units of temperature must be in kelvins.

Notice that each of the previous gas laws introduced, can be derived from the combined gas law:

At constant T, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* Boyle's Law: $P_1V_1 = P_2V_2$

At constant P, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* Charles's Law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

At constant V, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* Gay-Lussac's Law: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

In other words, if you know the equation for the combined gas law, you can calculate relationships between pressure, volume, or temperature of a fixed amount of gas.

Example 8.8.2

A sample of gas at an initial volume of 8.33 L, an initial pressure of 1.82 atm, and an initial temperature of 286 K simultaneously changes its temperature to 355 K and its volume to 5.72 L. What is the final pressure of the gas?

Solution

We can use the combined gas law directly; all the units are consistent with each other, and the temperatures are given in Kelvin. Substituting,

$$\frac{(1.82\,atm)(8.33\,L)}{286\,K} = \frac{P_2(5.72\,L)}{355\,K}$$

We rearrange this to isolate the P_2 variable all by itself. When we do so, certain units cancel:

$$\frac{(1.82\,atm)(8.33\;\cancel{L})(355\;\cancel{K})}{(286\;\cancel{K})(5.72\;\cancel{L})} = P_2$$

Multiplying and dividing all the numbers, we get

$$P_2 = 3.29\,atm$$

Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing.

Exercise 8.8.2

If P_1 = 662 torr, V_1 = 46.7 mL, T_1 = 266 K, P_2 = 409 torr, and T_2 = 371 K, what is V_2?

Answer

105 mL

Summary

- There are gas laws that relate any two physical properties of a gas.
- The combined gas law relates pressure, volume, and temperature of a gas.

Contributors

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8.9: Avogadro's Law - The Relation between Volume and Molar Amount

Learning Objectives

- Describe the relationship between the amount and volume of a gas, Avogadro's Law.
- Define the conditions of standard temperature and pressure.

The Relationship between Amount and Volume: Avogadro's Law

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure 8.9.1). This is the historic "Avogadro's hypothesis."

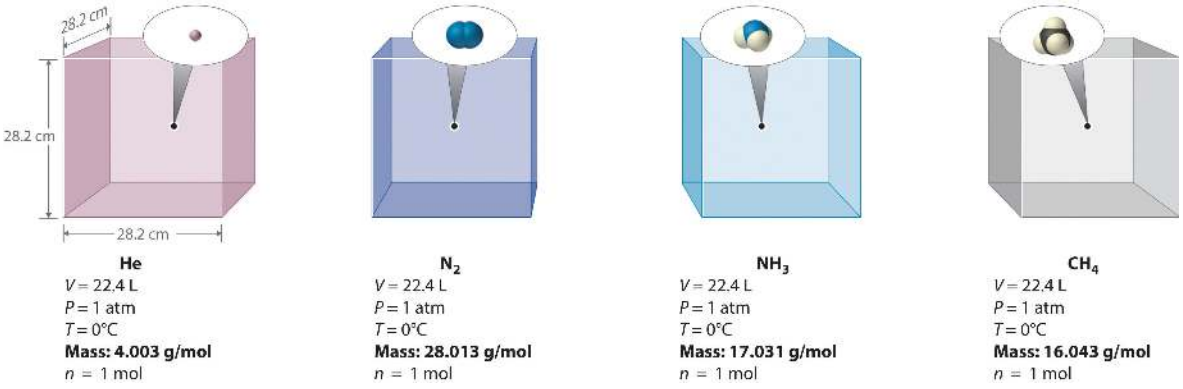


Figure 8.9.1: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

Because the number of particles is related to the number of moles (1 mol = 6.022×10^{23} particles), **Avogadro's law** essentially states that equal volumes of different gases, at the same temperature and pressure, contain the same *amount* (moles, particles) of gas. *At constant temperature and pressure, the volume (V) of a sample of gas is directly proportional to the number of moles (n) of gas in the sample.* Stated mathematically,

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V}{n} = k$$

where $\propto$ means "is proportional to," and *k* is a proportionality constant that is the same for all gases.

In terms of two sets of data: $\frac{V_1}{n_1} = \frac{V_2}{n_2}$.

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures. Mathematical relationships can also be determined for the other variable pairs, such as *P* versus *n*, and *n* versus *T*.

> *Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).*

Standard Temperature and Pressure

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure (STP)** is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to more directly compare the properties of gases that differ from one another.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\,atm)V = (1\,mol)\left(0.08205\frac{L.\,atm}{mol.\,K}\right)(273\,K)$$

All the units cancel except for L, the unit of volume. So V = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Figure 8.9.1). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

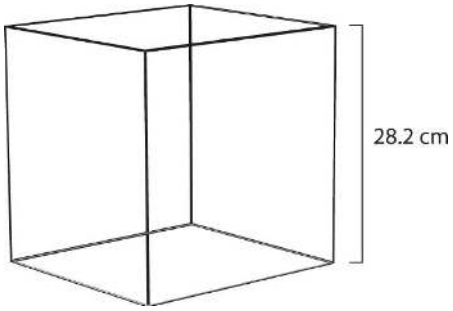


Figure 8.9.1: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

Example 8.9.4

How many moles of Ar are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7\ \cancel{L} \times \frac{1\,mol}{22.4\ \cancel{L}} = 1.73\,mol$$

Exercise 8.9.4

What volume does 4.87 mol of Kr have at STP?

Answer

109 L

Example 8.9.5

What volume of H_2 is produced at STP when 55.8 g of Zn metal react with excess HCl?

$$\mathrm{Zn(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)}$$

Solution

This is a stoichiometry problem with a twist: we need to use the molar volume of a gas at STP to determine the final answer. The first part of the calculation is the same as in a previous example:

$$55.8\ g\ \cancel{Zn} \times \frac{1\ mol\ \cancel{Zn}}{65.41\ g\ \cancel{Zn}} \times \frac{1\,mol\,H_2}{1\ mol\ \cancel{Zn}} = 0.853\,H_2$$

Now we can use the molar volume, 22.4 L/mol, because the gas is at STP:

$$0.853\ \cancel{mol\ H_2} \times \frac{22.4\ L}{1\ \cancel{mol\ H_2}} = 19.1\ L\ H_2$$

Alternatively, we could have applied the molar volume as a third conversion factor in the original stoichiometry calculation.

? Exercise 8.9.5

What volume of HCl is generated if 3.44 g of Cl_2 are reacted at STP?

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

Answer

2.17 L

Summary

- Avogadro's law states that the volume of gas is directly proportional to the number of moles of gas.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.
- At STP, gases have a volume of 22.4 L per mole.

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8.10: The Ideal Gas Law

Learning Objectives

- Describe the ideal gas law.
- Use the ideal gas law to calculate pressure, volume, temperature, or moles of an ideal gas.

So far, the gas laws we have considered have all required that the gas change its conditions; then we can predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So,

$$\frac{PV}{nT} = constant$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant. Indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R$$

which is usually rearranged as

$$PV = nRT$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant \(*R*\) is called the **ideal gas law constant**. Its value depends on the units used to express pressure and volume.

Table 8.10.1: Values of the Ideal Gas Law Constant lists the numerical values of R.

Numerical Value	Units
0.08205	$\frac{L \cdot atm}{mol \cdot K}$
62.36	$\frac{L \cdot torr}{mol \cdot K} = \frac{L \cdot mmHg}{mol \cdot K}$
8.314	$\frac{J}{mol \cdot K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and expression of the temperature in kelvin. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 8.10.1

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

The first step is to convert temperature to kelvins:

$$34 + 273 = 307\,\text{K}$$

Now we can substitute the conditions into the ideal gas law:

$$(1.21atm)(V) = (4.22\,mol)\left(0.08205\frac{L.\,atm}{mol.\,K}\right)(307\,K)$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V = \frac{(4.22)(0.08205)(307)}{1.21} L$$

Then solving for volume, we get V = 87.9 L

? Exercise 8.10.1

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

✓ Example 8.10.2

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332\ g\ \cancel{Hg} \times \frac{1\ mol\ Hg}{200.59\ g\ \cancel{Hg}} = 0.0000165\ mol = 1.65 \times 10^{-5} mol$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00332\ mm\ Hg)(435\ L) = (1.65 \times 10^{-5} mol)(62.36 \frac{L.\ mmHg}{mol.\ K})T$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating T on one side, we get

$$T = \frac{(0.00332)(435)}{(1.65 \times 10^{-5})(62.36)} K$$

Then solving for K, we get T = 1,404 K.

? Exercise 8.10.2

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

The ideal gas law can also be used in stoichiometry problems.

✓ Example 8.10.3

What volume of H_2 is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2\,HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H_2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H_2 is calculated:

$$55.8\ g\ \cancel{Zn} \times \frac{1\ mol\ \cancel{Zn}}{65.41\ g\ \cancel{Zn}} \times \frac{1\ mol\ H_2}{1\ mol\ \cancel{Zn}} = 0.853\ H_2$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07 atm)V = (0.853\ mol)\left(0.08205 \frac{L.\ atm}{mol.\ K}\right)(299\ K)$$

All the units cancel except for L, for volume, which means V = 19.6 L

? Exercise 8.10.3

What pressure of HCl is generated if 3.44 g of Cl_2 are reacted in 4.55 L at 455 K?

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

Answer

0.796 atm

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems with chemical reactions that involve gases.

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8.11: Partial Pressures and Dalton's Law

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8.12: Liquids

Learning Objective

- Define the vapor pressure of liquids.
- Explain the origin of both surface tension and capillary action.

There are some properties that all liquids, including water, have. All liquids have a certain portion of particles with enough energy to enter the gas phase, and if these particles are at the surface of the liquid, they do so (Figure 8.12.1). The formation of a gas from a liquid at temperatures below the boiling point is called **evaporation**. At these temperatures, the material in the gas phase is called **vapor**, rather than gas; the term *gas* is reserved for when the gas phase is the stable phase.

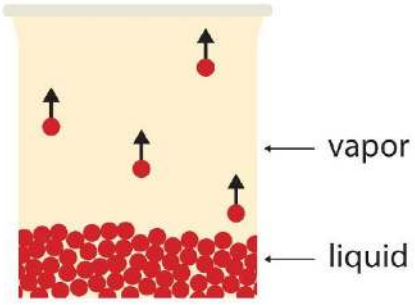


Figure 8.12.1: Evaporation. Some particles of a liquid have enough energy to escape the liquid phase to become a vapor.

If the available volume is large enough, eventually all the liquid will become vapor. But if the available volume is not enough, eventually some of the vapor particles will reenter the liquid phase (Figure 8.12.2 Equilibrium). At some point, the number of particles entering the vapor phase will equal the number of particles leaving the vapor phase, so there is no net change in the amount of vapor in the system. We say that the system is *at equilibrium*. The partial pressure of the vapor at equilibrium is called the **vapor pressure** of the liquid.

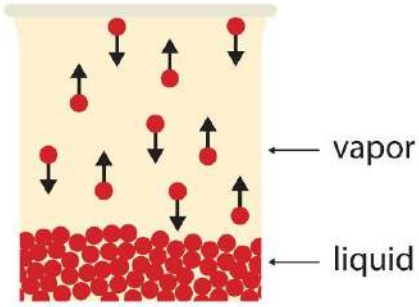


Figure 8.12.2: Equilibrium. At some point, the number of particles entering the vapor phase will be balanced by the number of particles returning to the liquid. This point is called equilibrium.

Understand that the liquid has not stopped evaporating. The reverse process—condensation—is occurring as fast as evaporation, so there is no net change in the amount of vapor in the system. The term *dynamic equilibrium* represents a situation in which a process still occurs, but the opposite process also occurs at the same rate, so that there is no net change in the system.

The vapor pressure for a substance is dependent on the temperature of the substance; as the temperature increases, so does the vapor pressure. Figure 8.12.3 - Plots of Vapor Pressure versus Temperature for Several Liquids, is a plot of vapor pressure versus temperature for several liquids. Having defined vapor pressure, we can also redefine the boiling point of a liquid: the temperature at which the vapor pressure of a liquid equals the surrounding environmental pressure. The **normal boiling point**, then, is the temperature at which the vapor pressure is 760 torr, or exactly 1 atm. Thus boiling points vary with surrounding pressure, a fact that can have large implications on cooking foods at lower- or higher-than-normal elevations. Atmospheric pressure varies significantly with altitude.

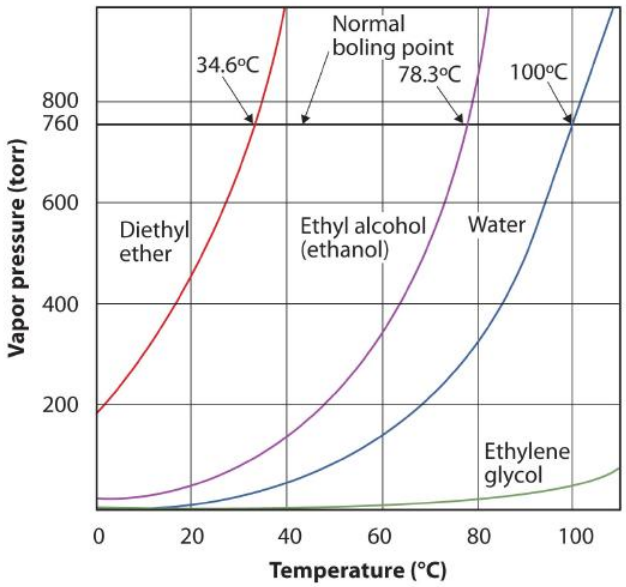


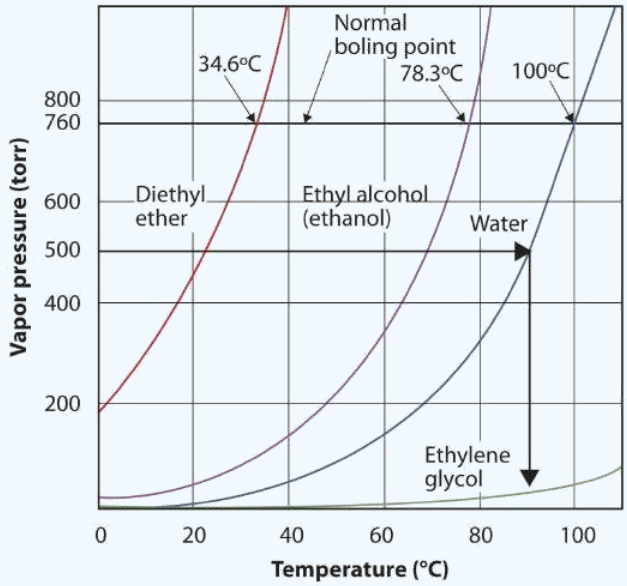
Figure 8.12.3: Plots of Vapor Pressure versus Temperature for Several Liquids. The vapor pressure of a liquid depends on the identity of the liquid and the temperature, as this plot shows.

Example 8.12.1

Use Figure 8.12.3to estimate the boiling point of water at 500 torr, which is the approximate atmospheric pressure at the top of Mount Everest.

Solution

See the accompanying figure. Five hundred torr is between 400 and 600, so we extend a line from that point on the *y*-axis across to the curve for water and then drop it down to the *x*-axis to read the associated temperature. It looks like the point on the water vapor pressure curve corresponds to a temperature of about 90°C, so we conclude that the boiling point of water at 500 torr is 90°C.



By reading the graph properly, you can estimate the boiling point of a liquid at different temperatures.

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? Exercise 8.12.1

Use Figure 8.12.3 to estimate the boiling point of ethanol at 400 torr.

Answer

about 65°C

The vapor pressure curve for water is not exactly zero at the melting point 0°C. Even ice has a vapor pressure—that is why it sublimes over time. However, the vapor pressures of solids are typically much lower than that of liquids. At −1°C, the vapor pressure of ice is 4.2 torr. At a freezer temperature of 0°F (−17°C), the vapor pressure of ice is only 1.0 torr; so-called deep freezers can get down to −23°C, where the vapor pressure of ice is only 0.6 torr.

All liquids share some other properties as well. **Surface tension** is an effect caused by an imbalance of forces on the atoms at the surface of a liquid, as shown in Figure 8.12.4. The blue particle in the bulk of the liquid experiences intermolecular forces from all around, as illustrated by the arrows. However, the yellow particle on the surface does not experience any forces above it because there are no particles above it. This leads to an imbalance of forces, called surface tension.

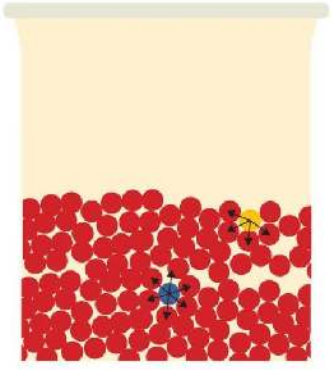


Figure 8.12.4 Surface Tension. Surface tension comes from the fact that particles at the surface of a liquid do not experience interactions from all directions, leading to an imbalance of forces on the surface.

Surface tension is responsible for several well-known behaviors of liquids, including water. Liquids with high surface tension tend to bead up when present in small amounts (Figure 8.12.5).



Figure 8.12.5 Effects of Surface Tension © Thinkstock. Water on the surface of this apple beads up due to the effect of surface tension.

Surface tension causes liquids to form spheres in free fall or zero gravity. Surface tension is also responsible for the fact that small insects can "walk" on water. Because of surface tension, it takes energy to break the surface of a liquid, and if an object (such as an insect) is light enough, there is not enough force due to gravity for the object to break through the surface, so the object stays on top of the water (Figure 8.12.6). Carefully done, this phenomenon can also be illustrated with a thin razor blade or a paper clip.



Figure 8.12.6 Walking on Water. Small insects can actually walk on top of water because of surface tension effects. (Unsplash License; Miguel Alcântara via unsplash)

The fact that small droplets of water bead up on surfaces does not mean that water—or any other liquid—does not interact with other substances. Sometimes the attraction can be very strong. **Adhesion** is the tendency of a substance to interact with other substances because of intermolecular forces, while **cohesion** is the tendency of a substance to interact with itself. If cohesive forces within a liquid are stronger than adhesive forces between a liquid and another substance, then the liquid tends to keep to itself; it will bead up. However, if adhesive forces between a liquid and another substance are stronger than cohesive forces, then the liquid will spread out over the other substance, trying to maximize the interface between the other substance and the liquid. It is said that the liquid *wets* the other substance.

Adhesion and cohesion are important for other phenomena as well. In particular, if adhesive forces are strong, then when a liquid is introduced to a small-diameter tube of another substance, the liquid will move up or down in the tube, as if ignoring gravity. Because tiny tubes are called capillaries, this phenomenon is called **capillary action.** For example, one type of capillary action, *capillary rise*, is seen when water or water-based liquids rise up in thin glass tubes (like the capillaries sometimes used in blood tests), forming an upwardly curved surface called a **meniscus**. Capillary action is also responsible for the "wicking" effect that towels and sponges use to dry wet objects; the matting of fibers forms tiny capillaries that have good adhesion with water. Cotton is a good material for this; polyester and other synthetic fabrics do not display similar capillary action, which is why you seldom find rayon bath towels. A similar effect is observed with liquid fuels or melted wax and their wicks. Capillary action is thought to be at least partially responsible for transporting water from the roots to the tops of trees, even tall ones.

On the other hand, some liquids have stronger cohesive forces than adhesive forces. In this case, in the presence of a capillary, the liquid is forced down from its surface; this is an example of a type of capillary action called *capillary depression*. In this case, the meniscus curves downward. Mercury has very strong cohesive forces; when a capillary is placed in a pool of mercury, the surface of the mercury liquid is depressed (Figure 8.12.7).

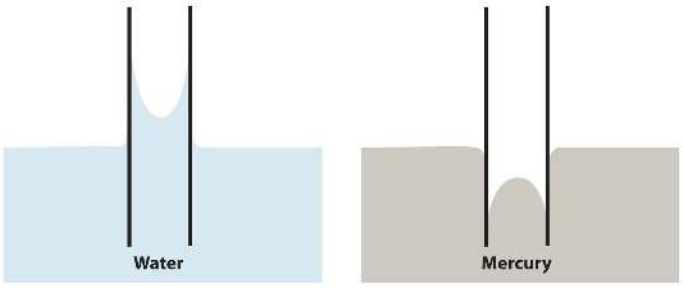


Figure 8.12.7: Capillary Action. (a) Capillary rise is seen when adhesion is strong, such as with water in a thin glass tube. (b) Capillary depression is seen when cohesive forces are stronger than adhesive forces, such as with mercury and thin glass tubes.

Chemistry is Everywhere: Waxing a Car

Responsible car owners are encouraged to wax their cars regularly. In addition to making the car look nicer, it also helps protect the surface, especially if the surface is metal. Why?

The answer has to do with cohesion and adhesion (and, to a lesser extent, rust). Water is an important factor in the rusting of iron, sometimes used extensively in outer car bodies. Keeping water away from the metal is one way to minimize rusting. A coat of paint helps with this. However, dirty or scratched paint can attract water, and adhesive forces will allow the water to wet the surface, maximizing its contact with the metal and promoting rust.



Figure 8.12.8: Waxing a car. Droplets of water on a freshly waxed car do not wet the car well because of low adhesion between water and the waxed surface. This helps protect the car from rust. (Unsplash License; Yuvraj Singh via Unspash)

Wax is composed of long hydrocarbon molecules that do not interact well with water. (Hydrocarbons are compounds with C and H atoms; for more information on hydrocarbons, see Chapter 16). That is, a thin layer of wax will not be wetted by water. A freshly waxed car has low adhesive forces with water, so water beads up on the surface, as a consequence of its cohesion and surface tension. This minimizes the contact between water and metal, thus minimizing rust.

Summary

- All liquids evaporate.
- If volume is limited, evaporation eventually reaches a dynamic equilibrium, and a constant vapor pressure is maintained.
- All liquids experience surface tension, an imbalance of forces at the surface of the liquid.
- All liquids experience capillary action, demonstrating either capillary rise or capillary depression in the presence of other substances.

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8.13: Solids

Learning Objective

- Describe the general properties of a solid.
- Describe the six different types of solids.

A solid is like a liquid in that particles are in contact with one another. Solids are unlike liquids in that the intermolecular forces are strong enough to hold the particles in place. At low enough temperatures, all substances are solids (helium is the lone exception), but the temperature at which the solid state becomes the stable phase varies widely among substances, from 20 K (−253°C) for hydrogen to over 3,900 K (3,600°C) for carbon.

The solid phase has several characteristics. First, solids maintain their shape. They do not fill their entire containers like gases do, and they do not adopt the shape of their containers like liquids do. They cannot be easily compressed like gases can, and they have relatively high densities.

Solids may also demonstrate a variety of properties. For example, many metals can be beaten into thin sheets or drawn into wires, while compounds such as NaCl will shatter if they are struck. Some metals, such as sodium and potassium, are rather soft, while others, such as diamond, are very hard and can easily scratch other substances. Appearances differ as well: most metals are shiny and silvery, but sulfur (a nonmetal) is yellow, and ionic compounds can take on a rainbow of colors. Solid metals conduct electricity and heat, while ionic solids do not. Many solids are opaque, but some are transparent. Some dissolve in water, but some do not. Figure 8.13.1, shows two solids that exemplify the similar and dissimilar properties of solids.



Figure 8.13.1: Properties of Solids. (a) Sodium metal is silvery, soft, opaque, and conducts electricity and heat well. (b) NaCl is transparent, hard, colorless, and does not conduct electricity or heat well in the solid state. These two substances illustrate the range of properties that solids can have. Source: Photo on left courtesy of Images of Elements, http://images-of-elements.com/sodium.php. Photo on right courtesy of Choba Poncho, commons.wikimedia.org/wiki/File:Sodiumchloride_crystal_01.jpg.

Solids can have a wide variety of physical properties. We will review the different types of solids and the bonding that gives them their properties.

First, we must distinguish between two general types of solids. An **amorphous solid** is a solid with no long-term structure or repetition. Examples include glass and many plastics, both of which are composed of long chains of molecules with no order from one molecule to the next. A **crystalline solid** is a solid that has a regular, repeating three-dimensional structure. A crystal of NaCl (Figure 8.13.1) is one example: at the atomic level, NaCl is composed of a regular three-dimensional array of Na^+ ions and Cl^- ions.

There is only one type of amorphous solid. However, there are several different types of crystalline solids, depending on the identity of the units that compose the crystal.

An **ionic solid** is a crystalline solid composed of ions (even if the ions are polyatomic). NaCl is an example of an ionic solid (Figure 8.13.2 - An Ionic Solid). The Na^+ ions and Cl^- ions alternate in three dimensions, repeating a pattern that goes on throughout the sample. The ions are held together by the attraction of opposite charges—a very strong force. Hence most ionic solids have relatively high melting points; for example, the melting point of NaCl is 801°C. Ionic solids are typically very brittle. To break them, the very strong ionic attractions need to be broken; a displacement of only about 1×10^{-10} m will move ions next

to ions of the same charge, which results in repulsion. Ionic solids do not conduct electricity in their solid state; however, in the liquid state and when dissolved in some solvent, they do conduct electricity. This fact originally promoted the idea that some substances exist as ionic particles.

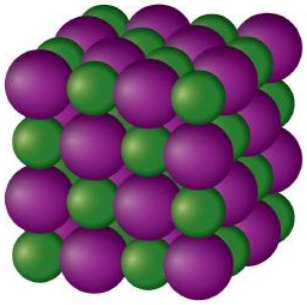


Figure 8.13.2: An Ionic Solid. NaCl is a solid composed of a three-dimensional array of alternating Na^+ ions (green) and Cl^- ions (purple) held together by the attraction of opposite charges.

A **molecular solid** is a crystalline solid whose components are covalently bonded molecules. Many molecular substances, especially when carefully solidified from the liquid state, form solids where the molecules line up with a regular fashion similar to an ionic crystal, but they are composed of molecules instead of ions. Because the intermolecular forces between molecules are typically less strong than in ionic solids, molecular solids typically melt at lower temperatures and are softer than ionic solids. Ice is an example of a molecular solid. In the solid state, the molecules line up in a regular pattern (Figure 8.13.3). Some very large molecules, such as biological molecules, will form crystals only if they are very carefully solidified from the liquid state or, more often, from a dissolved state; otherwise, they will form amorphous solids.

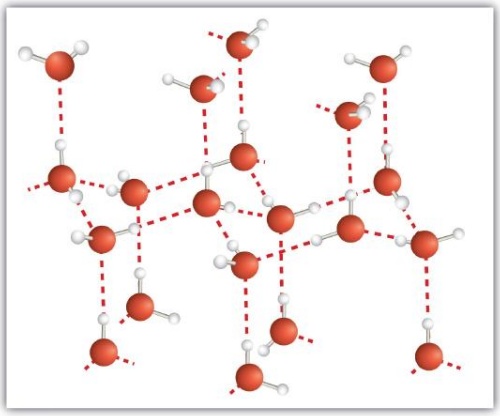


Figure 8.13.3: Molecular Solids. Water molecules line up in a regular pattern to form molecular solids. The dotted lines show how the polar O–H covalent bonds in one molecule engage in hydrogen bonding with other molecules. The O atoms are red, and the H atoms are white.

Some solids are composed of atoms of one or more elements that are covalently bonded together in a seemingly never-ending fashion. Such solids are called **covalent network solids**. Each piece of the substance is essentially one huge molecule, as the covalent bonding in the crystal extends throughout the entire crystal. The two most commonly known covalent network solids are carbon in its diamond form and silicon dioxide (SiO_2). Figure 8.13.4 - Covalent Network Solids, shows the bonding in a covalent network solid. Generally, covalent network solids are poor conductors of electricity, although their ability to conduct heat is variable: diamond is one of the most thermally conductive substances known, while SiO_2 is about 100 times less thermally conductive. Most covalent network solids are very hard, as exemplified by diamond, which is the hardest known substance. Covalent network solids have high melting points by virtue of their network of covalent bonds, all of which would have to be broken for them to transform into a liquid. Indeed, covalent network solids are among the highest-melting substances known: the melting point of diamond is over 3,500°C, while the melting point of SiO_2 is around 1,650°C. These characteristics are explained by the network of covalent bonds throughout the sample.

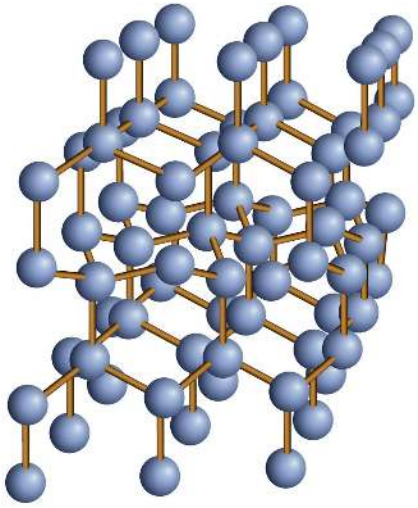


Figure 8.13.4: Covalent Network Solids. Diamond is a covalent network solid, with each C atom making four covalent bonds to four other C atoms. A diamond is essentially one huge molecule.

A **metallic solid** is a solid with the characteristic properties of a metal: shiny and silvery in color and a good conductor of heat and electricity. A metallic solid can also be hammered into sheets and pulled into wires. A metallic solid exhibits metallic bonding, a type of intermolecular interaction caused by the sharing of the *s* valence electrons by all atoms in the sample. It is the sharing of these valence electrons that explains the ability of metals to conduct electricity and heat well. It is also relatively easy for metals to lose these valence electrons, which explains why metallic elements usually form cations when they make compounds.

Example 8.13.1

Predict the type of crystal exhibited by each solid.

a. MgO
b. Ag
c. CO_2

Solution

a. A combination of a metal and a nonmetal makes an ionic compound, so MgO would exist as ionic crystals in the solid state.
b. Silver is a metal, so it would exist as a metallic solid in the solid state.
c. CO_2 is a covalently bonded molecular compound. In the solid state, it would form molecular crystals. (You can actually see the crystals in dry ice with the naked eye.)

Exercise 8.13.1

Predict the type of crystal exhibited by each solid.

a. I_2
b. $Ca(NO_3)_2$

Answers

a. molecular crystals
b. ionic crystals

Food and Drink Application: The Rocks We Eat

The foods and beverages we eat and drink all have different phases: solid, liquid, and gas. (How do we ingest gases? Carbonated beverages have gas, which sometimes cause a person to belch.) However, among the solids we eat, three in particular are, or are produced from, rocks. Yes, rocks!

The first one is NaCl, or common salt. Salt is the only solid that we ingest that is actually mined as a rock (hence the term *rock salt*; it really is a rock). Salt provides both Na^+ ions and Cl^- ions, both of which are necessary for good health. Salt preserves food, a function that was much more important before the days of modern food preparation and storage. The fact that saltiness is one of the major tastes the tongue can detect suggests a strong evolutionary link between ingesting salt and survival. There is some concern today that there is too much salt in the diet; it is estimated that the average person consumes at least three times as much salt daily as is necessary for proper bodily function.

The other two rocks we eat are related: sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3). However, we do not mine these substances directly from the ground; we mine trona, whose chemical formula is $Na_3H(CO_3)_2$. This substance is dissolved in water and treated with CO_2 gas to make either Na_2CO_3 or $NaHCO_3$. Another process, called the Solvay process, is also used to make Na_2CO_3. In the Solvay process, NH_3 and CO_2 are added to solutions of NaCl to make $NaHCO_3$ and NH_4Cl; the $NaHCO_3$ precipitates and is heated to produce Na_2CO_3. Either way, we get these two products from the ground (i.e., rocks).

$NaHCO_3$ is also known as baking soda, which is used in many baked goods. Na_2CO_3 is used in foods to regulate the acid balance. It is also used in laundry (where it is called washing soda) to interact with other ions in water that tend to reduce detergent efficiency.



Figure 8.13.5: Salt Mining © Thinkstock. Salt mining can be at the surface or below ground. Here salt is mined from surface deposits. Part of the processing facility can be seen in the background.

Summary

- Solids can be divided into amorphous solids and crystalline solids.
- Crystalline solids can be ionic, molecular, covalent network, or metallic.

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8.14: Changes of State Calculations

Learning Objectives

- Define enthalpy of fusion and enthalpy of vaporization.
- Calculate the energy changes that accompany phase changes.
- Interpret heating and cooling curves.

Everyday we take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine the changes in energy that occur during these changes in state or phase changes.

As introduced in an earlier section, changes of state involve changes in enthalpy ΔH, or changes in energy. Melting (changing a solid to liquid) and evaporating (changing a liquid to a gas) are both *endothermic* processes, requiring the addition of heat to break the intermolecular interactions between molecules. The reverse processes, condensation (changing a gas to a liquid) and freezing (changing a liquid to a solid), are both *exothermic*, meaning heat is given off or released when intermolecular interactions are reformed. The specific amount of energy absorbed or released when one gram of substance changes between a solid and a liquid (at the melting point) is called the **enthalpy of fusion** or heat of fusion, (ΔH_{fus}). At the boiling point, when one gram of substance changes between a liquid and a gas, the energy change is called the **enthalpy of vaporization** or heat of vaporization, (ΔH_{vap}).

Heating Curves

It is important to understand the difference between the energy associated with changes in temperature and changes in state where the temperature remains constant. This difference is most clearly depicted in a **heating curve**, which is a plot of the temperature versus heating time (or heat added). The heating curve in figure 8.14.1is the temperature change for a 75 g sample of water as heat is added over time. The sample is initially solid (ice) at 1 atm and −23°C; as heat is added, the *temperature* of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the amount of energy (in Joules or calories) required to raise the temperature of 1 g of ice by 1°C. As the temperature increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of liquid water is *greater* than that of solid water. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

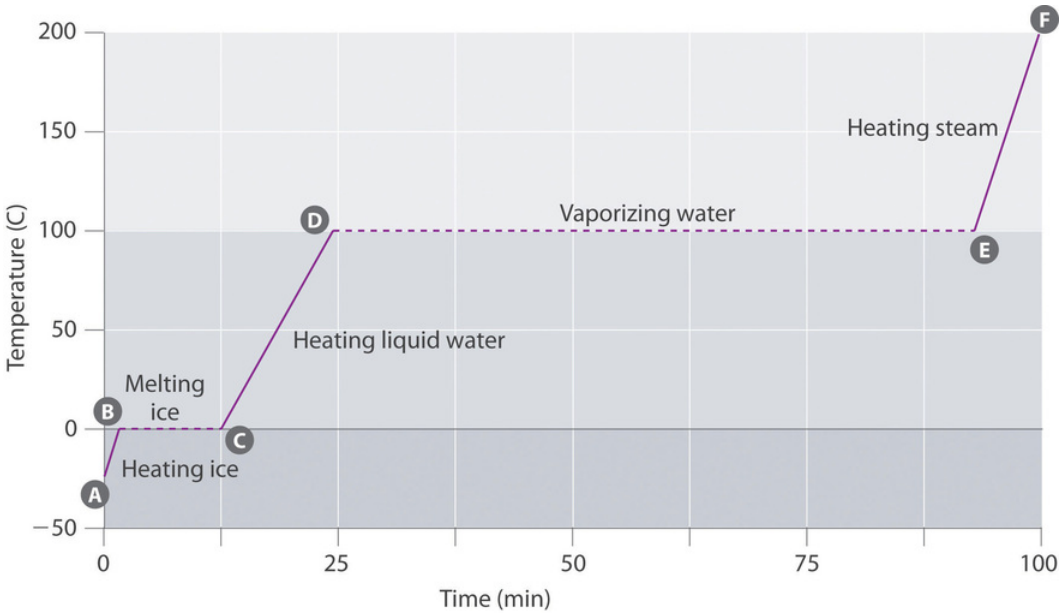


Figure 8.14.1: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

It is worth noting again that *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure 8.14.1, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 8.14.1, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The **cooling curve**, in Figure 8.14.2 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled (heat is released). Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 8.14.1, 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.

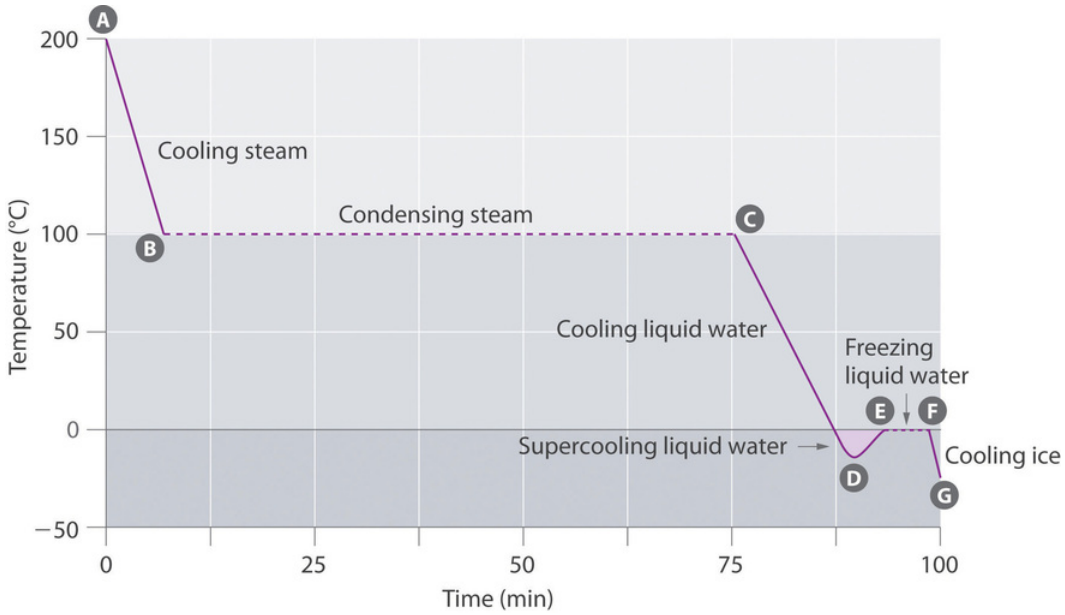


Figure 8.14.2: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.



A Video Discussing the Thermodynamics of Phase Changes. Video Source: The Thermodynamics of Phase Changes, YouTube(opens in new window) [youtu.be]

Example 8.14.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus}$$

For our 50.0 g ice cube:

$$\begin{aligned} q_{ice} &= 50.0g \cdot \frac{1\ mol}{18.02\ g} \cdot 6.01\ kJ/mol \\ &= 16.7\ kJ \end{aligned}$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$q_{tea} = -16,700J = 500mL \cdot \frac{1.00\ g}{1\ mL} \cdot 4.184J/(g\bullet{}^\circ C)\Delta T$$

$$\Delta T = -7.98^\circ C = T_f - T_i$$

$$T_f = 12.02^\circ C$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$\begin{aligned} q_{ice} &= -q_{tea} \\ q_{ice} &= m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g\bullet{}^\circ C) \cdot (T_f - 0.0^\circ C) \\ &= 209.2J/^\circ C \cdot T_f \end{aligned}$$

$$q_{tea} = m_{tea}C_s\Delta T = 500g \cdot 4.184J/(g\bullet{}^\circ C) \cdot (T_f - 12.02^\circ C) = 2092J/^\circ C \cdot T_f - 25,150J$$

$$209.2J/^\circ C \cdot T_f = -2092J/^\circ C \cdot T_f + 25,150J$$

$$2301.2J/^\circ C \cdot T_f = 25,150J$$

$$T_f = 10.9^\circ C$$

The final temperature is in between the initial temperatures of the tea (12.02 °C) and the melted ice (0.0 °C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

? Exercise 8.14.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 8.14.1

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Sublimation

There is also a phase change where a solid goes directly to a gas:

$$\text{solid} \rightarrow \text{gas} \tag{8.14.1}$$

This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO_2). At −78.5°C (−109°F), solid carbon dioxide sublimes, changing directly from the solid phase to the gas phase:

$$CO_2(s) \xrightarrow{-78.5^\circ C} CO_2(g) \tag{8.14.2}$$

Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it does directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C, solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimes, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimes, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a "burn," and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer's temperature and by wrapping foods tightly so water does not have any space to sublime into.

Summary

- Phase changes are associated with energy changes.
- The enthalpy of fusion, ΔH_{fus}, is the energy absorbed or released when a substance changes between a solid and a liquid.
- The enthalpy of vaporization, ΔH_{vap}, is the energy absorbed or released when a substance changes between a liquid and a gas.
- Heating and cooling curves are useful tools to show how temperature, energy, and phases are related.

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CHAPTER OVERVIEW

9: Solutions

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9.1: Mixtures and Solutions

Learning Objectives

- Describe the difference between homogenous and heterogenous mixtures.
- Distinguish a homogenous mixture as a solution or colloid.

As introduced previously, *mixtures* are combinations of two or more substances that each retain their individual physical properties. A mixture can be classified as either *heterogenous* or *homogenous*. In a heterogeneous mixture, the composition is *not* uniform throughout the sample, and sometimes the individual substances that make up the mixture can be differentiated by eye. Trail mix, salad, and blood (which is also called a suspension) are examples of heterogenous mixtures. Homogenous mixtures are uniform and have the same composition throughout. Air, simple syrup, and seawater are examples of homogenous mixtures.

Homogenous mixtures can be further classified, based on the *size* of their particles, as solutions or colloids. **Solutions** are composed of particles the size of an ion or small molecule, ~0.1-2.0 nm. The examples provided above are all considered solutions; air is a solution of small gas molecules, simple syrup is a solution of sucrose in water, and seawater is a solution of ions and water. Homogenous mixtures with larger particles, ~2.0-500 nm, are classified as **colloids**. Milk, fog, and butter are all considered colloids. Mixtures with particles larger than 500 nm are called **suspensions** and are considered to be heterogenous mixtures in which the particles will settle upon standing. Many medications are classified as suspensions that need to be re-mixed before taking in order to redistribute the particles throughout the mixture. Some examples and distinguishing characteristics of solutions, colloids, and suspensions are listed in Table 9.1.1 below.

Table 9.1.1: Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute. For example, in a solution of salt in water, the solute is salt, and solvent is water.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table 9.1.2 lists some common types of solutions, with examples of each.

Table 9.1.2: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages

Solvent Phase	Solute Phase	Example
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	saltwater
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

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9.2: The Solution Process

Learning Objectives

- Predict solubility based on interactions between solute and solvent.

What occurs at the molecular level to cause a solute to dissolve in a solvent? The answer depends in part on the strength of attractions between solute and solvent particles. A good rule of thumb is to use is *like dissolves like*, which means that substances must have similar intermolecular attractions to form solutions.

A substance can *dissolve* in a solvent, and form a solution, if the solute and solvent are *attracted* to each other. For example, water molecules that are held together by hydrogen bonding will dissolve solutes that can also hydrogen bond, like ethanol (CH_3CH_2OH). The new hydrogen bonds between the water and the ethanol molecules (solvent-solute attractions) are nearly as strong as the hydrogen bonds in water (solvent-solvent) and ethanol (solute-solute) alone, making the process of solution formation (also called dissolution or dissolving) favorable.

In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, are surrounded by solvent molecules. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called **solvation** and is illustrated in Figure 9.2.1. When the solvent is water, the word **hydration**, rather than solvation, is used.

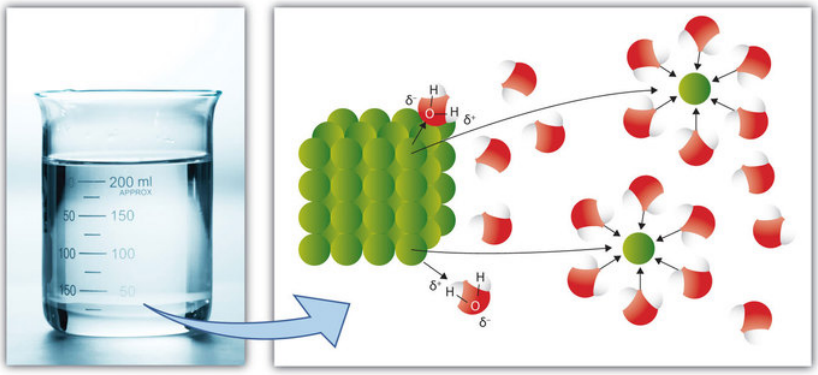


Figure 9.2.1: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

When a solute and solvent that do not have similar intermolecular interactions are mixed, a solution is not formed because the solute-solute or solvent-solvent attractions are stronger than any favorable interactions between solute and solvent. For example when water and oil are mixed, stay in separate layers, i.e., they will not mix to yield solutions and the water molecules remain hydrogen bonded to water molecules while the oil molecules stay together (Figure 9.2.2). Hydrogen bonding is the dominant intermolecular attractive force present in liquid water; the nonpolar hydrocarbon molecules of cooking oils are not capable of hydrogen bonding, instead being held together by dispersion forces. Forming an oil-water solution would require overcoming the very strong hydrogen bonding in water, as well as the significantly strong dispersion forces between the relatively large oil molecules. And, since the polar water molecules and nonpolar oil molecules would not experience very strong intermolecular attraction, very little energy would be released by solvation.



Figure 9.2.2: A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: Gautam Dogra).

Ionic Compounds and Covalent Compounds as Solutes

In the case of molecular solutes like glucose, the solute particles are individual molecules. However, if the solute is ionic, the individual ions separate from each other and become surrounded by solvent particles. The positively charged cations are attracted to the neg and anions of an ionic solute separate when the solute dissolves. This process is referred to as **dissociation** (Figure 9.2.1).

The dissociation of soluble ionic compounds gives solutions of these compounds an interesting property: they conduct electricity. Because of this property, soluble ionic compounds are referred to as electrolytes. Many ionic compounds dissociate completely and are therefore called **strong electrolytes**. Sodium chloride is an example of a strong electrolyte. Some compounds dissolve but dissociate only partially, and solutions of such solutes may conduct electricity only weakly. These solutes are called **weak electrolytes**. Acetic acid (CH_3COOH), the compound in vinegar, is a weak electrolyte. Solutes that dissolve into individual neutral molecules without dissociation do not impart additional electrical conductivity to their solutions and are called nonelectrolytes. Table sugar ($C_{12}H_{22}O_{11}$) is an example of a nonelectrolyte.

> *The term **electrolyte** is used in medicine to mean any of the important ions that are dissolved in aqueous solution in the body. Important physiological electrolytes include Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^-.*

Example 9.2.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

1. potassium chloride (KCl)
2. fructose ($C_6H_{12}O_6$)
3. isopropyl alcohol [$CH_3CH(OH)CH_3$]
4. magnesium hydroxide [$Mg(OH)_2$]

Solution

Each substance can be classified as an ionic solute or a nonionic solute. Ionic solutes are electrolytes, and nonionic solutes are nonelectrolytes.

1. Potassium chloride is an ionic compound; therefore, when it dissolves, its ions separate, making it an electrolyte.
2. Fructose is a sugar similar to glucose. (In fact, it has the same molecular formula as glucose.) Because it is a molecular compound, we expect it to be a nonelectrolyte.
3. Isopropyl alcohol is an organic molecule containing the alcohol functional group. The bonding in the compound is all covalent, so when isopropyl alcohol dissolves, it separates into individual molecules but not ions. Thus, it is a nonelectrolyte
4. Magnesium hydroxide is an ionic compound, so when it dissolves it dissociates. Thus, magnesium hydroxide is an electrolyte.

Exercise 9.2.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

a. acetone (CH_3COCH_3)
b. iron(III) nitrate [$Fe(NO_3)_3$]
c. elemental bromine (Br_2)
d. sodium hydroxide (NaOH)

Answer

a. nonelectrolyte

b. electrolyte

c. nonelectrolyte

d. electrolyte

Electrolytes in Body Fluids

Our body fluids are solutions of electrolytes and many other things. The combination of blood and the circulatory system is the *river of life*, because it coordinates all the life functions. When the heart stops pumping in a heart attack, the life ends quickly. Getting the heart restarted as soon as one can is crucial in order to maintain life.

The primary electrolytes required in the body fluid are cations (of calcium, potassium, sodium, and magnesium) and anions (of chloride, carbonates, aminoacetates, phosphates, and iodide). These are nutritionally called **macrominerals**.

Electrolyte balance is crucial to many body functions. Here's some extreme examples of what can happen with an imbalance of electrolytes: elevated potassium levels may result in cardiac arrhythmias; decreased extracellular potassium produces paralysis; excessive extracellular sodium causes fluid retention; and decreased plasma calcium and magnesium can produce muscle spasms of the extremities.

When a patient is dehydrated, a carefully prepared (commercially available) electrolyte solution is required to maintain health and well being. In terms of child health, oral electrolyte is given when a child is dehydrated due to diarrhea. The use of oral electrolyte maintenance solutions, which is responsible for saving millions of lives worldwide over the last 25 years, is one of the most important medical advances in protecting the health of children in the century, explains Juilus G.K. Goepp, MD, assistant director of the Pediatric Emergency Department of the Children's Center at Johns Hopkins Hospital. If a parent provides an oral electrolyte maintenance solution at the very start of the illness, dehydration can be prevented. The functionality of electrolyte solutions is related to their properties, and interest in electrolyte solutions goes far beyond chemistry.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are they performance and endurance enhancers like they claim? Who should drink them?

Typically, eight ounces of a sports drink provides between fifty and eighty calories and 14 to 17 grams of carbohydrate, mostly in the form of simple sugars. Sodium and potassium are the most commonly included electrolytes in sports drinks, with the levels of these in sports drinks being highly variable. The American College of Sports Medicine says a sports drink should contain 125 milligrams of sodium per 8 ounces as it is helpful in replenishing some of the sodium lost in sweat and promotes fluid uptake in the small intestine, improving hydration.

Gatorade

In the summer of 1965, the assistant football coach of the University of Florida Gators requested scientists affiliated with the university study why the withering heat of Florida caused so many heat-related illnesses in football players and provide a solution to increase athletic performance and recovery post-training or game. The discovery was that inadequate replenishment of fluids, carbohydrates, and electrolytes was the reason for the “wilting” of their football players. Based on their research, the scientists concocted a drink for the football players containing water, carbohydrates, and electrolytes and called it “Gatorade.”



In the next football season the Gators were nine and two and won the Orange Bowl. The Gators' success launched the sports-drink industry, which is now a multibillion-dollar industry that is still dominated by Gatorade.

University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors, Robert Cade.

Concept Review Exercise

1. Explain how the solvation process describes the dissolution of a solute in a solvent.

Answer

1. Each particle of the solute is surrounded by particles of the solvent, carrying the solute from its original phase.

Key Takeaway

- When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

Exercises

1. Describe what happens when an ionic solute like Na_2SO_4 dissolves in a polar solvent.
2. Describe what happens when a molecular solute like sucrose ($C_{12}H_{22}O_{11}$) dissolves in a polar solvent.
3. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
   a. NH_4NO_3
   b. CO_2
   c. NH_2CONH_2
   d. HCl
4. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
   a. $CH_3CH_2CH_2OH$
   b. $Ca(CH_3CO_2)_2$
   c. I_2
   d. KOH
5. Will solutions of each solute conduct electricity when dissolved?
   a. $AgNO_3$
   b. $CHCl_3$
   c. $BaCl_2$
   d. Li_2O
6. Will solutions of each solute conduct electricity when dissolved?
   a. CH_3COCH_3
   b. $N(CH_3)_3$
   c. $CH_3CO_2C_2H_5$
   d. $FeCl_2$

Answers

1. Each ion of the ionic solute is surrounded by particles of solvent, carrying the ion from its associated crystal.

2. Each sucrose molecule is surrounded by solvent molecules (attracted to each other via intermolecular forces of attraction).

3. a. electrolyte
   b. nonelectrolyte
   c. nonelectrolyte

d. electrolyte

4.

a. nonelectrolyte
b. electrolyte
c. nonelectrolyte
d. electrolyte

5.

a. yes
b. no
c. yes
d. yes

6.

a. no
b. no
c. no
d. yes

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9.3: Solubility

Learning Objectives

- Describe solutions as saturated or unsaturated by understanding solubility.

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 whose meanings depend on various factors.

Solubility

There is usually a limit to how much solute will dissolve in a given amount of solvent. This limit is called the **solubility** of the solute. Some solutes have a very small solubility, while other solutes are soluble in all proportions. Table 9.3.1 lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table 9.3.1 includes the temperature at which the solubility was determined.

Table 9.3.1: Solubilities of Various Solutes in Water at 25°C (Except as Noted)

Substance	Solubility (g in 100 mL of H_2O)
AgCl(s)	0.019
$C_6H_6(\ell)$ (benzene)	0.178
$CH_4(g)$	0.0023
$CO_2(g)$	0.150
$CaCO_3(s)$	0.058
$CaF_2(s)$	0.0016
$Ca(NO_3)_2(s)$	143.9
$C_6H_{12}O_6$ (glucose)	120.3 (at 30°C)
KBr(s)	67.8
$MgCO_3(s)$	2.20
NaCl(s)	36.0
$NaHCO_3(s)$	8.41
$C_{12}H_{22}O_{11}$ (sucrose)	204.0 (at 20°C)

If a solution contains so much solute that its solubility limit is reached, the solution is said to be **saturated**, and its concentration is known from information contained in Table 9.3.1. If a solution contains less solute than the solubility limit, it is **unsaturated**. Under special circumstances, more solute can be dissolved even after the normal solubility limit is reached; such solutions are called ***supersaturated*** and are not stable. If the solute is solid, excess solute can easily recrystallize. If the solute is a gas, it can bubble out of solution uncontrollably, like what happens when you shake a soda can and then immediately open it.

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution that will be discussed in later sections.

Solution Equilibrium

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (Figure 9.3.1*a*). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called crystallization. The **equilibrium** between dissolution and crystallization continue as long as excess solid is present, resulting in a

dynamic equilibrium analogous to the equilibrium that maintains the vapor pressure of a liquid. We can represent these opposing processes as follows:

$$solute + solvent \underset{crystallization}{\overset{dissolution}{\rightleftharpoons}} solution$$

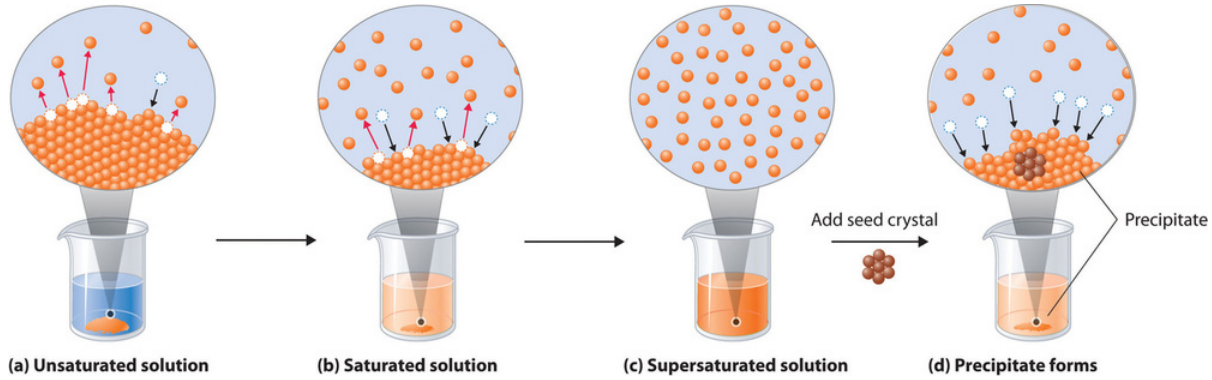


Figure 9.3.1: Dissolution and Precipitation. (a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

Starting on the left the solution starts are unsaturated, then saturated, then supersaturated, when seed crystal is added a precipitate forms.

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9.4: The Effect of Temperature on Solubility

Learning Objectives

- Describe how temperature affects solubility of different types of solute.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a **solubility curve**, a graph of the solubility vs. temperature (Figure $9.4.1$ below).

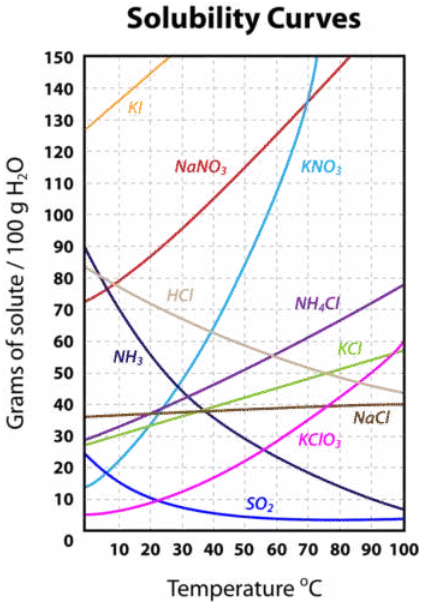


Figure 9.4.1: A solubility curve is a graph of the solubility of a substance as a function of temperature.

Notice how the temperature dependence of NaCl is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of NaCl. The curve for $\mathrm{KNO_3}$, on the other hand, is very steep, and so an increase in temperature dramatically increases the solubility of $\mathrm{KNO_3}$.

Several substances—HCl, $\mathrm{NH_3}$, and $\mathrm{SO_2}$—have solubility that decreases as temperature increases. They are all gases at standard pressure. When a solvent with a gas dissolved in it is heated, the kinetic energy of both the solvent and solute increase. As the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the attraction of the solvent molecules and return to the gas phase. Therefore, the solubility of a gas decreases as the temperature increases.

Solubility curves can be used to determine if a given solution is *saturated* or *unsaturated*. Suppose that 80 g of $\mathrm{KNO_3}$ is added to 100 g of water at $30\,^\circ\mathrm{C}$. According to the solubility curve in Figure $9.4.1$, approximately 48 g of $\mathrm{KNO_3}$ will dissolve at $30\,^\circ\mathrm{C}$. This means that the solution will be saturated since 48 g is less than 80 g. We can also determine that there will be $80 - 48 = 32$ g of undissolved $\mathrm{KNO_3}$ remaining at the bottom of the container. In a second scenario, suppose that this saturated solution is heated to $60\,^\circ\mathrm{C}$. According to the curve, the solubility of $\mathrm{KNO_3}$ at $60\,^\circ\mathrm{C}$ is about 107 g. The solution, in this case, is unsaturated since it contains only the original 80 g of dissolved solute. Suppose in a third case, that the solution is cooled all the way down to $0\,^\circ\mathrm{C}$. The solubility at $0\,^\circ\mathrm{C}$ is about 14 g, meaning that $80 - 14 = 66$ g of the $\mathrm{KNO_3}$ will recrystallize.

Supersaturated Solutions

Some solutes, such as sodium acetate, do not recrystallize easily. Suppose an exactly saturated solution of sodium acetate is prepared at $50\,^\circ\mathrm{C}$. As it cools back to room temperature, no crystals appear in the solution, even though the solubility of sodium acetate is lower at room temperature. A **supersaturated solution** is a solution that contains more than the maximum amount of solute that is capable of being dissolved at a given temperature. The recrystallization of the excess dissolved solute in a supersaturated solution can be initiated by the addition of a tiny crystal of solute, called a seed crystal. The seed crystal provides a nucleation site on which the excess dissolved crystals can begin to grow. Recrystallization from a supersaturated solution is typically very fast.



Chemistry in Everyday Life: Handwarmers

Recrystallization of excess solute from a supersaturated solution usually gives off energy as heat. Commercial heat packs, such as the one in Figure 9.4.2, containing supersaturated sodium acetate ($NaC_2H_3O_2$) take advantage of this phenomenon. You can probably find them at your local drugstore.



Figure 9.4.2: This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is "clicked." (credit: modification of work by "Velela"/Wikimedia Commons)

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9.5: The Effect of Pressure on Solubility - Henry's Law

Learning Objectives

- Describe how pressure affects concentration of a solute in a solution.

Pressure has very little effect on the solubility of solids or liquids, but has a significant effect on the solubility of gases. Gas solubility increases as the partial pressure of a gas above the liquid increases. Suppose a certain volume of water is in a closed container with the space above it occupied by carbon dioxide gas at standard pressure. Some of the $\mathrm{CO_2}$ molecules come into contact with the surface of the water and dissolve into the liquid. Now suppose that more $\mathrm{CO_2}$ is added to the space above the container, causing a pressure increase. In this case, more $\mathrm{CO_2}$ molecules are in contact with the water and so more of them dissolve. Thus, the solubility increases as the pressure increases. As with a solid, the $\mathrm{CO_2}$ that is undissolved reaches an equilibrium with the dissolved $\mathrm{CO_2}$, represented by the equation:

$$\mathrm{CO_2}\,(g) \rightleftharpoons \mathrm{CO_2}\,(aq)$$

At equilibrium, the rate of gaseous $\mathrm{CO_2}$ dissolution is equal to the rate of dissolved $\mathrm{CO_2}$ coming out of the solution.

When carbonated beverages are packaged, they are done so under high $\mathrm{CO_2}$ pressure so that a large amount of carbon dioxide dissolves in the liquid. When the bottle is open, the equilibrium is disrupted because the $\mathrm{CO_2}$ pressure above the liquid decreases. Immediately, bubbles of $\mathrm{CO_2}$ rapidly exit the solution and escape out of the top of the open bottle, see Figure $9.5.1$. The amount of dissolved $\mathrm{CO_2}$ decreases. If the bottle is left open for an extended period of time, the beverage becomes "flat" as more and more $\mathrm{CO_2}$ comes out of the liquid.

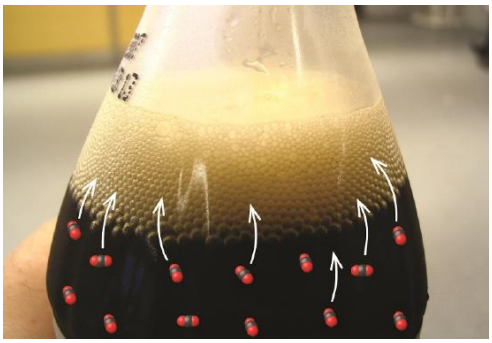


Figure $9.5.1$: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

The relationship of gas solubility to pressure is described by Henry's law, named after English chemist William Henry (1774-1836). **Henry's Law** states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. Henry's law can be written as follows:

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} = k$$

C_1 and P_1 are the concentration and the pressure at an initial set of conditions; C_2 and P_2 are the concentration and pressure at another changed set of conditions; k is a constant at a constant temperature. The solubility of a gas is typically reported in $\mathrm{g/L}$.

Example $9.5.1$

The solubility of a certain gas in water is $0.745\ \mathrm{g/L}$ at standard pressure. What is its solubility when the pressure above the solution is raised to $4.50\ \mathrm{atm}$? The temperature is constant at $20^{\circ}\mathrm{C}$.

Solution

Step 1: List the known quantities and plan the problem.

Known

- $C_1 = 0.745\ \mathrm{g/L}$

- $P_1 = 1.00\ \text{atm}$
- $P_2 = 4.50\ \text{atm}$

Unknown

Substitute into Henry's law and solve for C_2.

Step 2: Solve.

$$C_2 = \frac{C_1 \times P_2}{P_1} = \frac{0.745\ \text{g/L} \times 4.50\ \text{atm}}{1.00\ \text{atm}} = 3.35\ \text{g/L}$$

Step 3: Think about your result.

The solubility is increased to 4.5 times its original value, according to the direct relationship.

Exercise 9.5.1

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45 × 10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer

7.25 × 10^{-3} g in 100.0 mL or 0.0725 g/L

Case Study: Decompression Sickness ("The Bends")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.



Figure 9.5.4: (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.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 9.5.4).

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9.6: Units of Concentration

Learning Objectives

- Calculate concentration of a solution using different units.
- Use concentration units to calculate the amount of solute in a solution.
- Use molarity to determine quantities in chemical reactions.

Percent Concentrations

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:

$$\%\ \mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

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.

Example 9.6.1

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:

$$\%\ \mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

Exercise 9.6.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer

7.90%

For gases and liquids, volumes are relatively easy to measure, so the concentration of a liquid or a gas solution can be expressed as a **volume/volume percent** (% v/v): the volume of a solute divided by the volume of a solution times 100:

$$\%\ \mathrm{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

Again, the units of the solute and the solution must be the same. A hybrid concentration unit, **mass/volume percent** (% m/v), is commonly used for intravenous (IV) fluids (Figure 9.6.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\%\ \mathrm{m/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$$



Figure 9.6.1: Mass/Volume Percent.The 0.9% NaCl concentration on this IV bag is mass/volume percent (left). Such solution is used for other purposes and available in bottles (right). Figures used with permission from Wikipedia

Using Percent Concentration in Calculations

The percent concentration can be used to produce a conversion factor between the amount of solute and the amount of solution. As such, concentrations can be useful in a variety of stoichiometry problems as discussed in Chapter 6. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

As an example, if the given concentration is 5% *v/v* alcohol, this means that there are 5 mL of alcohol dissolved in every 100 mL solution.

$$\textbf{5 mL alcohol = 100 mL solution}$$

The two possible conversion factors are written as follows:

$$\frac{\textbf{5 mL alcohol}}{\textbf{100 mL solution}} \text{ or } \frac{\textbf{100 mL solution}}{\textbf{5 mL alcohol}}$$

Use the first conversion factor to convert from a given amount of solution to amount of solute. The second conversion factor is used to convert from a given amount of solute to amount of solution. Given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

Example 9.6.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

Solution

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\%\ \text{v/v} \rightarrow \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}}$$

That is, there are 45 mL of C_2H_5OH for every 100 mL of solution. We can use this fraction as a conversion factor to determine the amount of C_2H_5OH in 115 mL of solution:

$$115 \text{ mL solution} \times \frac{45 \text{ mL } C_2H_5OH}{100 \text{ mL solution}} = 51.8 \text{ mL } C_2H_5OH$$

? Exercise 9.6.2

What volume of a 12.75% m/v solution of glucose ($C_6H_{12}O_6$) in water is needed to obtain 50.0 g of $C_6H_{12}O_6$?

Answer

$$50.0 \text{ g } C_6H_12O_6 \times \frac{100 \text{ mL solution}}{12.75 \text{ g } C_6H_12O_6} = 392 \text{ mL solution}$$

✓ Example 9.6.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?

Solution

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

$$1 \text{ L} = 1{,}000 \text{ mL}$$

Because this is an exact relationship, it does not affect the significant figures of our result.

$$\%\text{ m/v} = \frac{9.0 \text{ g NaCl}}{1{,}000 \text{ mL solution}} \times 100\% = 0.90\%\text{ m/v}$$

? Exercise 9.6.3

The chlorine bleach that you might find in your laundry room is typically composed of 27.0 g of sodium hypochlorite (NaOCl), dissolved to make 500.0 mL of solution. What is the mass/volume percent of the bleach?

Answer

$$\%\text{ m/v} = \frac{27.0 \text{ g NaOCl}}{500.0 \text{ mL solution}} \times 100\% = 5.40\%\text{ m/v}$$

Parts per Million (ppm) and Parts per Billion (ppb)

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1{,}000{,}000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1{,}000{,}000{,}000$$

> *Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).*

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

> *In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.*

Example 9.6.4

If the concentration of cobalt in a human body is 21 ppb, what mass in grams of Co is present in a body having a mass of 70.0 kg?

Solution

A concentration of 21 ppb means "21 g of solute per 1,000,000,000 g of solution." Written as a **conversion factor,** this concentration of Co is as follows:

$$21 \text{ ppb Co} \rightarrow \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}}$$

We can use this as a conversion factor, but first we must convert 70.0 kg to gram units:

$$70.0 \text{ kg} \times \frac{1,000 \text{ g}}{1 \text{ kg}} = 7.00 \times 10^4 \text{ g}$$

Now we determine the amount of Co:

$$7.00 \times 10^4 \text{ g solution} \times \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}} = 0.0015 \text{ g Co}$$

This is only 1.5 mg.

Exercise 9.6.4

An 85 kg body contains 0.012 g of Ni. What is the concentration of Ni in parts per million?

Answer

0.14 ppm

Mole/Volume Concentration: Molarity

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. 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.

Molarity*(M)* is defined as the number of moles of a solute dissolved per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

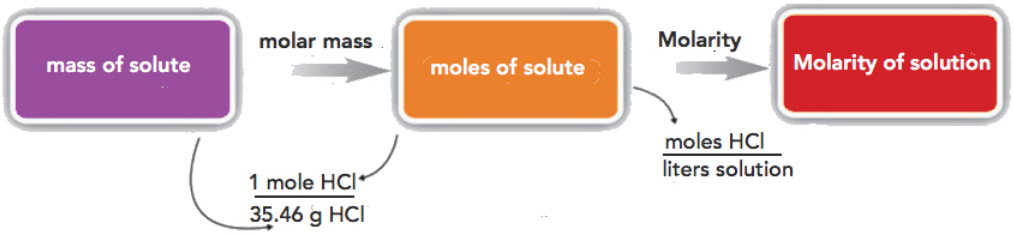
Molarity is abbreviated M (often referred to as "molar"), and the units are often abbreviated as mol/L. It is important to remember that "mol" in this expression refers to moles of solute and that "L" refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

which is read as "three point oh molar sodium chloride." Sometimes (aq) is added when the solvent is water, as in "3.0 M NaCl(aq)."

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.

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: convert the mass of solute to moles using the molar mass of HCl (36.46 g/mol):

$$22.4\ \cancel{gHCl} \times \frac{1\ mol\ HCl}{36.46\ \cancel{gHCl}} = 0.614\ mol\ HCl$$

Step 2: use the definition of molarity to determine the concentration:

$$M\ =\ \frac{0.614\ mol\ HCl}{1.56 L\ solution} = 0.394\ MHCl$$

Example 9.6.5

What is the molarity of an aqueous solution of 25.0 g of NaOH in 750 mL?

Solution

Before we substitute these quantities into the definition of molarity, we must convert them to the proper units. The mass of NaOH must be converted to moles of NaOH. The molar mass of NaOH is 40.00 g/mol:

$$25.0\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 0.625\ \text{mol NaOH}$$

Next, we convert the volume units from milliliters to liters:

$$750\ \text{mL} \times \frac{1\ \text{L}}{1,000\ \text{mL}} = 0.750\ \text{L}$$

Now that the quantities are expressed in the proper units, we can substitute them into the definition of molarity:

$$\text{M} = \frac{0.625\ \text{mol NaOH}}{0.750\ \text{L}} = 0.833\ \text{M NaOH}$$

Exercise 9.6.5

If a 350 mL cup of coffee contains 0.150 g of caffeine ($C_8H_{10}N_4O_2$), what is the molarity of this caffeine solution?

Answer

0.00221 M

Using Molarity in Calculations

The definition of molarity can also be used to calculate a needed volume of solution, given its concentration and the number of moles desired, or the number of moles of solute (and subsequently, the mass of the solute), given its concentration and volume. As in the percent concentration, molarity can also be expressed as a conversion factor.

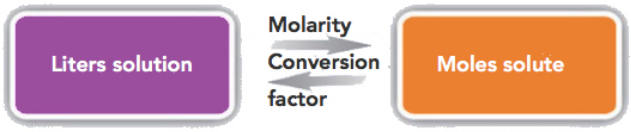
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a 3.0 M solution of sucrose means that there are three moles of sucrose dissolved in every liter of solution. Mathematically, this is stated as follows:

3.0 moles sucrose = 1 L solution

Dividing both sides of this expression by either side, we generate two possible conversion factors:

$$\frac{\textbf{3.0 mol sucrose}}{\textbf{1 L solution}} \text{ or } \frac{\textbf{1 L solution}}{\textbf{3.0 mol sucrose}}$$

The first conversion factor can be used to convert from *volume (L) of solution to moles solute*, and the *second converts from moles of solute to volume (L) of solution*.



For example, suppose we are asked how many moles of sucrose are present in 0.108 L of a 3.0 M sucrose solution. The given volume (0.108 L) is multiplied by the first conversion factor to cancel the L units, and find that 0.32 moles of sucrose are present.

$$0.108\ L\ \cancel{solution} \times \frac{3.0\ mol\ sucrose}{1 L\ \cancel{solution}} = 0.32\ mol\ sucrose$$

How many liters of 3.0 M sucrose solution are needed to obtain 4.88 mol of sucrose? In such a conversion, we multiply the given (4.88 moles sucrose) with the second conversion factor. This cancels the moles units and converts it to liters of solution.

$$4.88\ mol\ \cancel{sucrose} \times \frac{1\ L\ solution}{3.0\ \cancel{mol\ sucrose}} = 1.63\ L\ solution$$

Example 9.6.6

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

1. To solve for the volume, multiply the "given" (0.450 mol of dimethylamine) with the molarity conversion factor (0.0753 M). Use the proper conversion factor to cancel the unit "mol" and get the unit volume (L) of solution:

$$0.450\ \text{mol dimethylamine} \times \frac{1\ \text{L solution}}{0.0753\ \text{mol dimethylamine}} = 5.98\ \text{L solution}$$

2. The strategy in solving this problem is to convert the given volume (5.00 L) using the 6.00 M (conversion factor) to solve for moles of ethylene glycol, which can then be converted to grams.

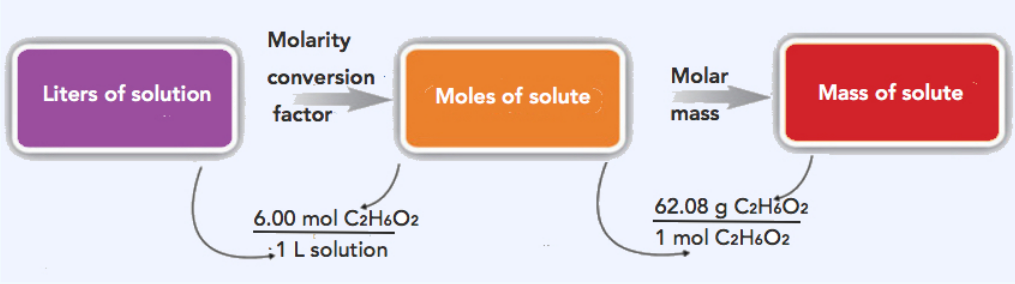
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} = 30.0\ \text{mol}\ C_2H_6O_2$$

Step 2: Convert 30.0 mols $C_2H_6O_2$ to grams $C_2H_6O_2$. Molar mass of $C_2H_6O_2$= 62.08 g/mol

$$30.0\ \text{mol}\ C_2H_6O_2 \times \frac{62.08\ \text{g}\ C_2H_6O_2}{1\ \text{mol}\ C_2H_6O_2} = 1,860\ \text{g}\ C_2H_6O_2$$

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:



$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} \times \frac{62.08\ \text{g}\ C_2H_6O_2}{1\ \text{mol}\ C_2H_6O_2} = 1,860\ \text{g}\ C_2H_6O_2$$

The final answer is rounded off to 3 significant figures. Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Note: Dimethylamine has a “fishy” odor. In fact, organic compounds called amines cause the odor of decaying fish.

? Exercise 9.6.6

a. What volume of a 0.0902 M solution of formic acid (HCOOH) is needed to obtain 0.888 mol of HCOOH?
b. Acetic acid ($HC_2H_3O_2$) is the acid in vinegar. How many grams of $HC_2H_3O_2$ are in 0.565 L of a 0.955 M solution?

Answer

a. 9.84 L

b. 32.4 g

Solution Stoichiometry

Of all the ways of expressing concentration, molarity is the one most commonly used in stoichiometry problems because it is directly related to the mole unit. Consider the following chemical equation:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Suppose we want to know how many liters of aqueous HCl solution will react with a given mass of NaOH. A typical approach to answering this question is as follows:

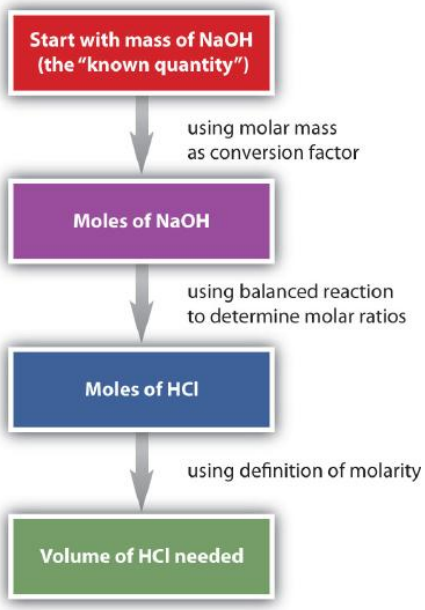


***Figure* 9.6.2**: *Typical approach to solving Molarity problems*

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving.

✓ Example 9.6.7

How many milliliters of a 2.75 M HCl solution are needed to react with 185 g of NaOH? The balanced chemical equation for this reaction is as follows:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Solution

We will follow the flowchart to answer this question. First, we convert the mass of NaOH to moles of NaOH using its molar mass, 40.00 g/mol:

$$185\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 4.63\ \text{mol NaOH}$$

Using the balanced chemical equation, we see that there is a one-to-one ratio of moles of HCl to moles of NaOH. We use this to determine the number of moles of HCl needed to react with the given amount of NaOH:

$$4.63\ \text{mol NaOH} \times \frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}} = 4.63\ \text{mol HCl}$$

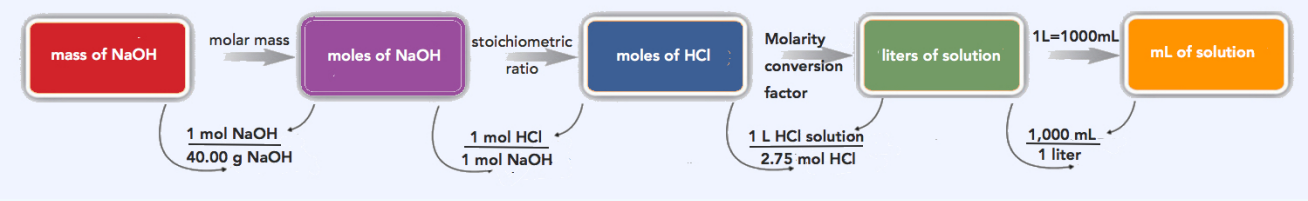
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$2.75\ \text{M HCl} = \frac{4.63\ \text{mol HCl}}{\text{volume of HCl solution}}$$

$$\text{volume of HCl} = \frac{4.63\ \text{mol HCl}}{2.75\ \text{M HCl}} = 1.68\ \text{L} \times \frac{1,000\ \text{mL}}{1\ \text{L}} = 1,680\ \text{mL}$$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

The same multi-step problem can also be worked out in a single line, rather than as separate steps, as follows:



$$185\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} \times \frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}} \times \frac{1\ \text{L HCl solution}}{2.75\ \text{mol HCl}} \times \frac{1000\ \text{mL HCl solution}}{1\ \text{L HCl solution}} = 1,680\ \text{mL HCl solution}$$

Our final answer (rounded off to three significant figures) is 1,680 mL HCl solution.

Exercise 9.6.7

How many milliliters of a 1.04 M H_2SO_4 solution are needed to react with 98.5 g of $Ca(OH)_2$? The balanced chemical equation for the reaction is as follows:

$$H_2SO_{4(aq)} + Ca(OH)_{2(s)} \rightarrow 2H_2O_{(\ell)} + CaSO_{4(aq)}$$

Answer

1,280 mL

The generic steps for performing stoichiometry problems such as this are shown in Figure 9.6.3. You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure 9.6.3 indicate that you can start at either end of the chart and, after a series of simple conversions, determine the quantity at the other end.

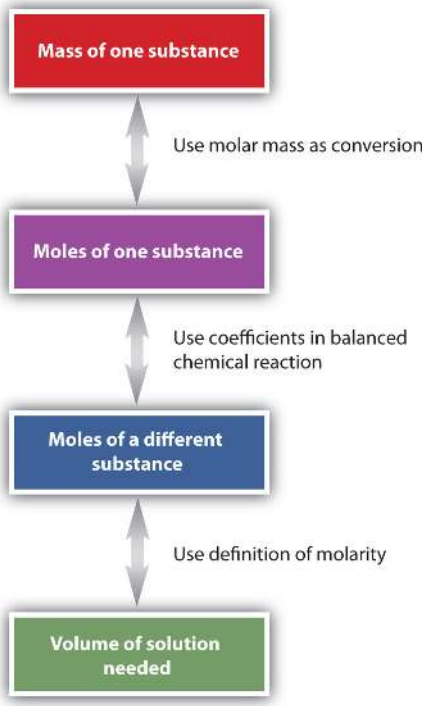


Figure 9.6.3: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Solutions in Our Body

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table 9.6.1 lists the typical concentrations of some of these solutes.

Table 9.6.1: Approximate Concentrations of Various Solutes in Some Solutions in the Body*

Solution	Solute	Concentration (M)
blood plasma	Na^+	0.138
	K^+	0.005
	Ca^{2+}	0.004
	Mg^{2+}	0.003
	Cl^-	0.110
	HCO_3^-	0.030
stomach acid	HCl	0.10
urine	NaCl	0.15
	PO_4^{3-}	0.05
	NH_2CONH_2 (urea)	0.30

*Note: Concentrations are approximate and can vary widely.

Looking Closer: The Dose Makes the Poison

Why is it that we can drink 1 qt of water when we are thirsty and not be harmed, but if we ingest 0.5 g of arsenic, we might die? There is an old saying: *the dose makes the poison*. This means that what may be dangerous in some amounts may not be dangerous in other amounts.

Take arsenic, for example. Some studies show that arsenic deprivation limits the growth of animals such as chickens, goats, and pigs, suggesting that arsenic is actually an essential trace element in the diet. Humans are constantly exposed to tiny amounts of arsenic from the environment, so studies of completely arsenic-free humans are not available; if arsenic is an essential trace mineral in human diets, it is probably required on the order of 50 ppb or less. A toxic dose of arsenic corresponds to about 7,000 ppb and higher, which is over 140 times the trace amount that may be required by the body. Thus, arsenic is not poisonous in and of itself. Rather, it is the amount that is dangerous: the dose makes the poison.

Similarly, as much as water is needed to keep us alive, too much of it is also risky to our health. Drinking too much water too fast can lead to a condition called water intoxication, which may be fatal. The danger in water intoxication is not that water itself becomes toxic. It is that the ingestion of too much water too fast dilutes sodium ions, potassium ions, and other salts in the bloodstream to concentrations that are not high enough to support brain, muscle, and heart functions. Military personnel, endurance athletes, and even desert hikers are susceptible to water intoxication if they drink water but do not replenish the salts lost in sweat. As this example shows, even the right substances in the wrong amounts can be dangerous!

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9.7: Dilution

Learning Objective

- Calculate the concentration of solutions prepared by dilution.

Often, a worker will need to change the concentration of a solution by changing the amount of solvent. **Dilution** is the *addition of solvent*, which decreases the concentration of the solute in the solution. **Concentration** is the *removal of solvent*, which increases the concentration of the solute in the solution. (Do not confuse the two uses of the word *concentration* here!)

In both dilution and concentration, the amount of solute stays the same. This gives us a way to calculate what the new solution volume must be for the desired concentration of solute. From the definition of molarity,

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

we can solve for the number of moles of solute:

moles of solute = Molarity (mol/L) x Volume of solution (L)

A simpler way of writing this is to use M to represent molarity and V to represent volume. So the equation becomes

moles of solute = $M \times V$

Because this quantity does not change before and after the change in concentration, the product MV must be the same before and after the concentration change. Using numbers to represent the initial and final conditions, we have

$$M_1V_1 = M_2V_2$$

as the dilution equation. The volumes must be expressed in the same units. Note that this equation gives only the initial and final conditions, not the amount of the change. The amount of change in volume is determined by subtraction.

mple

If 25.0 mL of a 2.19 M solution are diluted to 72.8 mL, what is the final concentration?

Solution

It does not matter which set of conditions is labeled 1 or 2, as long as the conditions are paired together properly. Using the dilution equation, we have

(2.19 M)(25.0 mL) = M_2(72.8 mL)

Solving for the second concentration (noting that the milliliter units cancel),

M_2 = 0.752 M

The concentration of the solution has decreased. In going from 25.0 mL to 72.8 mL, 72.8 − 25.0 = 47.8 mL of solvent must be added.

rcise

A 0.885 M solution of KBr whose initial volume is 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

Concentrating solutions involves removing solvent. Usually this is done by evaporating or boiling, assuming that the heat of boiling does not affect the solute. The dilution equation is used in these circumstances as well.

Chemistry is Everywhere: Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.



Figure 9.7.1 Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is easy to calculate how much stock solution to use:

$$(10\%)V_1 = (0.50\%)(100\text{ mL})V_1 = 5\text{ mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

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9.8: Ions in Solution - Electrolytes

Learning Objectives

- Define solutes as strong electrolytes, weak electrolytes, or nonelectrolytes.
- Calculate equivalents for an ionic solute.

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called electrolytes. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a **weak electrolyte**.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 9.8.1).

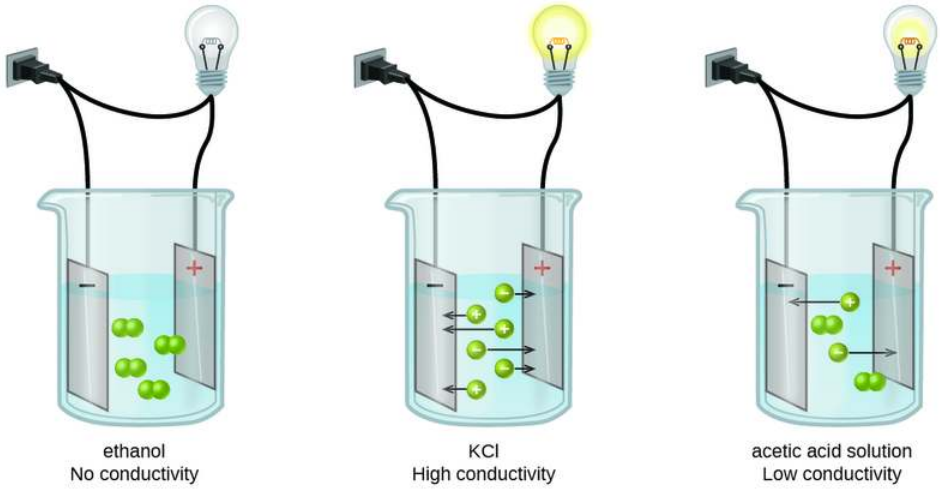


Figure 9.8.1: Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 9.8.2. 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.

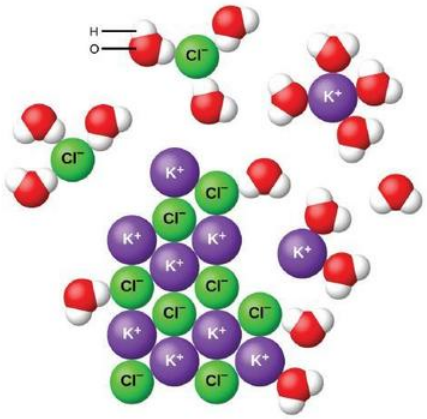


Figure 9.8.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

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 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).

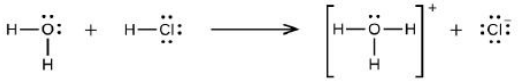
Covalent Electrolytes

Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton to another molecule of water, yielding hydronium and hydroxide ions.

$$H_2O(l)^+H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{9.8.1}$$

In some cases, we find that solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, when we dissolve hydrogen chloride in water, we find that the solution is a very good conductor. The water molecules play an essential part in forming ions: Solutions of hydrogen chloride in many other solvents, such as benzene, do not conduct electricity and do not contain ions.

Hydrogen chloride is an *acid*, and so its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. Acids and bases will be explored further in a later chapter.

Equivalents

Concentrations of ionic solutes are occasionally expressed in units called equivalents (Eq). One equivalent equals 1 mol of positive or negative charge. Thus, 1 mol/L of $Na^+(aq)$ is also 1 Eq/L because sodium has a 1+ charge. A 1 mol/L solution of $Ca^{2+}(aq)$ ions has a concentration of 2 Eq/L because calcium has a 2+ charge. Dilute solutions may be expressed in milliequivalents (mEq)—for example, human blood plasma has a total concentration of about 150 mEq/L.

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9.9: 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 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 9.9.1.

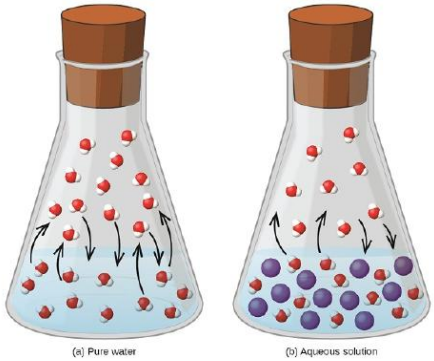


Figure 9.9.1: Vapor Pressure Depression. The presence of solute particles blocks some of the ability for liquid particles to evaporate. Thus, solutions of solid solutes typically have a lower vapor pressure than the pure solvent.

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.

$$\Delta T_{boiling} = mol\ particles \times 0.51^\circ C$$

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.

Everyday Application: Adding Salt to Pasta Water

When cooking dried pasta, many recipes call for salting the water before cooking the pasta. Some argue—with colligative properties on their side—that adding salt to the water raises the boiling point, thus cooking the pasta faster. Is there any truth to this?



Figure 9.9.2: Cooking dried pasta. Why do so many recipes call for adding salt to water when boiling pasta? Is it to raise the boiling temperature of the water? (Public Domain; Jan Vašek via pixabay)

In order to increase the boiling temperature of 4 L of water by 1.0°C, with the presumption that dried pasta cooks noticeably faster at 101°C than at 100°C (although a 1° difference may make only a negligible change in cooking times), over 1 lb of salt (~1 cup) would be needed. In your experience, do you add almost a cup of salt to a pot of water to make pasta? Certainly not! A few pinches, perhaps one-fourth of a teaspoon, but not almost a cup! It is obvious that the little amount of salt that most people add to their pasta water is not going to significantly raise the boiling point of the water.

So why do people add some salt to boiling water? There are several possible reasons, the most obvious of which is taste: adding salt adds a little bit of salt flavor to the pasta. It cannot be much because most of the salt remains in the water, not in the cooked pasta. However, it may be enough to detect with our taste buds. The other obvious reason is habit; recipes tell us to add salt, so we do, even if there is little scientific or culinary reason to do so.

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.

$$\Delta T_{freezing} = mol\ particles \times -1.86\,^{\circ}C$$

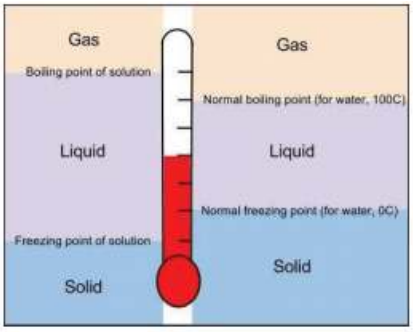


Figure 9.9.3: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

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 9.9.4). 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 9.9.4: 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

✔ Example 9.9.1

Which solution's freezing point deviates more from that of pure water—a 1 M solution of NaCl or a 1 M solution of $CaCl_2$?

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 $CaCl_2$ dissolves, it separates into three ions—one Ca^{2+} ion and two Cl^- ions. Thus, mole for mole, $CaCl_2$ will have 50% more impact on freezing point depression than NaCl.

? Exercise 9.9.1

Which solution's boiling point deviates more from that of pure water—a 1 M solution of $CaCl_2$ or a 1 M solution of $MgSO_4$?

Answer

$CaCl_2$

✔ Example 9.9.2

Estimate the boiling point of 0.2 M $CaCl_2$ solution.

Solution

The boiling point increases 0.51°C for every mole of solute per liter of water. For this estimation, let's assume that 1 liter of solution is roughly the same volume as 1 liter of water. A 0.2 M $CaCl_2$ solution contains 0.2 moles of $CaCl_2$ solution formula units per liter of solution. Each $CaCl_2$ unit separates into three ions.

$$0.2 \text{ mol } CaCl_2 \times \frac{3 \text{ mol ions}}{1 \text{ mol } CaCl_2} \times \frac{0.51^\circ C}{1 \text{ mol ion}} = 0.306^\circ C$$

The normal boiling point of water is 100°C, so the boiling point of the solution is raised to 100.31°C.

? Exercise 9.9.2

Estimate the freezing point of 0.3 M $CaCl_2$ solution.

Answer

–1.7°C

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9.10: Osmosis and Osmotic Pressure

Learning Objectives

- Describe osmosis and how it relates to osmotic pressure.

Osmotic Pressure

The last colligative property of solutions we will consider is a very important one for biological systems. It involves **osmosis**, the process by which solvent molecules can pass through certain membranes but solute particles cannot. When two solutions of different concentration are present on either side of these membranes (called *semipermeable membranes*), there is a tendency for solvent molecules to move from the more dilute solution to the more concentrated solution until the concentrations of the two solutions are equal. This tendency is called **osmotic pressure**. External pressure can be exerted on a solution to counter the flow of solvent; the pressure required to halt the osmosis of a solvent is equal to the osmotic pressure of the solution.

Consider the apparatus illustrated in Figure 9.10.1, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as osmosis.

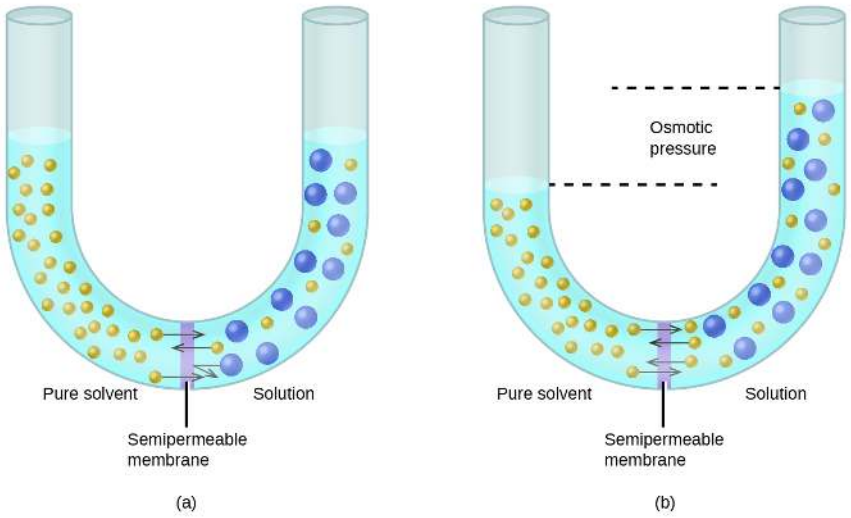


Figure 9.10.1: Osmosis results in the transfer of solvent molecules from a sample of low (or zero) solute concentration to a sample of higher solute concentration.

When osmosis is carried out in an apparatus like that shown in Figure 9.10.1, the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the osmotic pressure (π) of the solution. The osmotic pressure of a dilute solution can be determined in a similar way the pressure of an ideal gas is calculated using the ideal gas law:

$$\pi = \left(\frac{n}{V}\right) RT$$

where n is the number of moles of particles in solution, V is the volume, and R is the universal gas constant.

Osmolarity (osmol) is a way of reporting the total number of particles in a solution to determine osmotic pressure. It is defined as the molarity of a solute times the number of particles a formula unit of the solute makes when it dissolves (represented by i):

$$osmol = M \times i$$

If more than one solute is present in a solution, the individual osmolarities are additive to get the total osmolarity of the solution. Solutions that have the same osmolarity have the same osmotic pressure. If solutions of differing osmolarities are present on opposite sides of a semipermeable membrane, solvent will transfer from the lower-osmolarity solution to the higher-osmolarity solution. Counterpressure exerted on the high-osmolarity solution will reduce or halt the solvent transfer. An even higher pressure can be exerted to force solvent from the high-osmolarity solution to the low-osmolarity solution, a process called *reverse osmosis*. Reverse osmosis is used to make potable water from saltwater where sources of fresh water are scarce.

Example 9.10.1

A 0.50 M NaCl aqueous solution and a 0.30 M $Ca(NO_3)_2$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Solution

The solvent will flow into the solution of higher osmolarity. The NaCl solute separates into two ions—Na^+ and Cl^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol (NaCl)} = 0.50\ \text{M} \times 2 = 1.0\ \text{osmol}$$

The $Ca(NO_3)_2$ solute separates into three ions—one Ca^{2+} and two NO_3^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol } [Ca(NO_3)_2] = 0.30\ \text{M} \times 3 = 0.90\ \text{osmol}$$

The osmolarity of the $Ca(NO_3)_2$ solution is lower than that of the NaCl solution, so water will transfer through the membrane from the $Ca(NO_3)_2$ solution to the NaCl solution.

Exercise 9.10.1

A 1.5 M $C_6H_{12}O_6$ aqueous solution and a 0.40 M $Al(NO_3)_3$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Answer

osmol $C_6H_{12}O_6$ = 1.5; osmol $Al(NO_3)_3$ = 1.6

The solvent flows from $C_6H_{12}O_6$ solution (lower osmolarity) to $Al(NO_3)_3$ solution (higher osmolarity).

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solutes in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be isotonic with blood serum. If a *less* concentrated solution, a **hypotonic** solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture (Figure 9.10.2*a*). This process is called hemolysis. When a *more* concentrated solution, a **hypertonic** solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called *crenation* (Figure 9.10.2*c*). Only if red blood cells are placed in **isotonic** solutions that have the same osmolarity as exists inside the cells are they unaffected by negative effects of osmotic pressure (Figure 9.10.2*b*). Glucose solutions of about 0.31 M, or sodium chloride (NaCl) solutions of about 0.16 M, are isotonic with blood plasma.

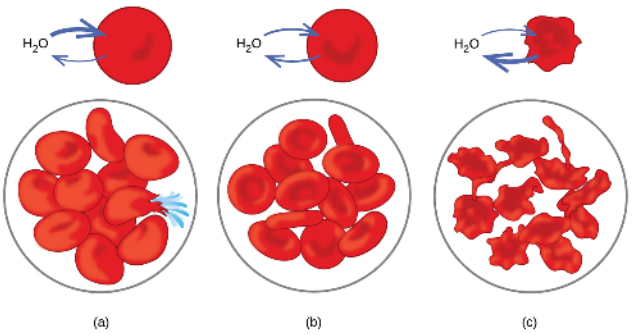


Figure 9.10.2: Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a **hypotonic** solution; (b) maintain normal volume and shape in an **isotonic** solution; and (c) shrivel and possibly die in a **hypertonic** solution. (credit a/b/c: modifications of work by "LadyofHats"/Wikimedia commons)

Note: Isotonic Solutions for Red Blood Cells

The concentration of an red blood cell isotonic solution made with sodium chloride (NaCl) is half that of an isotonic solution made with glucose (0.16 M and 0.31 M respectively). This is because NaCl produces *two ions* when a formula unit dissolves, while molecular glucose produces only *one particle* when a formula unit dissolves. The osmolarities are therefore the same even though the concentrations of the two solutions are different.

isotonic NaCl solution: $osmol = 0.16\ M \times 2 = 0.32\ osmol/L$

isotonic glucose solution: $osmol = 0.31\ M \times 1 = 0.31\ osmol/L$

Osmotic pressure explains why you should not drink seawater if you are abandoned in a life raft in the middle of the ocean. Its osmolarity is about three times higher than most bodily fluids. You would actually become thirstier as water from your cells was drawn out to dilute the salty ocean water you ingested. Our bodies do a better job coping with hypotonic solutions than with hypertonic ones. The excess water is collected by our kidneys and excreted.

Osmotic pressure effects are used in the food industry to make pickles from cucumbers and other vegetables and in brining meat to make corned beef. It is also a factor in the mechanism of getting water from the roots to the tops of trees!

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9.11: Dialysis

Learning Objectives

- Understand the difference between dialysis and osmosis.

As introduced in a previous section, osmosis is the process by which *solvent* particles can pass through a semipermeable membrane. **Dialysis** is similar to osmosis with the difference being that the pores in the semipermeable membranes are larger, thus allowing *both* solvent and small solute molecules to pass through. Larger solute particles, such as colloids and proteins, that cannot pass through the pores in the membrane are left behind. The size of the pores in the semipermeable membranes can be varied to allow for separation (or purification) of specific solute molecules from a solution based on their size. Biochemists and molecular biologists use dialysis to purify proteins from mixtures or to change the concentration of solute particles for different types of experiments, as illustrated in Figure 9.11.1.

Figure 9.11.1: Dialysis separates colloidal particles like protein and starch from water, small molecules, and ions. Source: Potcherboy at English Wikipedia / CC BY (https://creativecommons.org/licenses/by/3.0)

Role of dialysis in the human body

Kidneys filter the blood by dialysis, which occurs in tubular structures called nephrons (Figure 9.11.2. The nephrons filter the water, and small molecules, like glucose, amino acids, urea, and ions from the blood. Useful products and most of the water reabsorb later on, but urea and other waste products are excreted through urine. (You can read more about kidney structure and function here.)

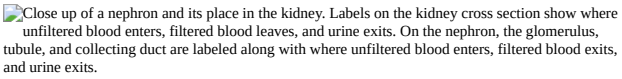


Figure 9.11.2: Image of a close up nephron and its place in the kidney. Labels on the kidney cross section show where unfiltered blood enters, filtered blood leaves, and urine exits. On the nephron, the glomerulus, tubule, and collecting duct are labeled along with where unfiltered blood enters, filtered blood exits, and urine exits. (National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health. CC0 1.0)

The main function of the kidneys is to filter the blood to remove wastes and extra water, which are then expelled from the body as urine. Some diseases rob the kidneys of their ability to perform this function, causing a buildup of waste materials in the bloodstream. If a kidney transplant is not available or desirable, a procedure called dialysis can be used to remove waste materials and excess water from the blood.

In one form of dialysis, called **hemodialysis**, (see Figure 9.11.3), a patient's blood is passed though a length of tubing that travels through an *artificial kidney machine* (also called a *dialysis machine*). In the dialyser, a section of tubing composed of cellophane (a semipermeable membrane) is immersed in dialysate, a solution of sterile water, glucose, amino acids, and certain electrolytes. The osmotic pressure of the blood forces waste molecules, such as urea, and excess water through the membrane into the dialysate. Red and white blood cells are too large to pass through the membrane, so they remain in the blood. After being cleansed in this way, the blood is returned to the body.

Dialysis is a continuous process, as the osmosis of waste materials and excess water takes time. Typically, 5–10 lb of waste-containing fluid is removed in each dialysis session, which can last 2–8 hours and must be performed several times a week. Although some patients have been on dialysis for 30 or more years, dialysis is always a temporary solution because waste materials are constantly building up in the bloodstream. A more permanent solution is a kidney transplant.



Figure 9.11.3: Simplified hemodialysis circuit. (Yassine Mrabet, CC BY 3.0)

Career Connection: Dialysis Technician

Dialysis is a medical process of removing wastes and excess water from the blood by diffusion and ultrafiltration. When kidney function fails, dialysis must be done to artificially rid the body of wastes. This is a vital process to keep patients alive. In some cases, the patients undergo artificial dialysis until they are eligible for a kidney transplant. In others who are not candidates for kidney transplants, dialysis is a life-long necessity.

Dialysis technicians typically work in hospitals and clinics. While some roles in this field include equipment development and maintenance, most dialysis technicians work in direct patient care. Their on-the-job duties, which typically occur under the direct supervision of a registered nurse, focus on providing dialysis treatments. This can include reviewing patient history and current condition, assessing and responding to patient needs before and during treatment, and monitoring the dialysis process. Treatment may include taking and reporting a patient's vital signs and preparing solutions and equipment to ensure accurate and sterile procedures.

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CHAPTER OVERVIEW

10: Acids and Bases

10.1: Acids and Bases Definitions
10.2: Acid and Base Strength
10.3: Acid Dissociation Constants
10.4: Water as Both an Acid and a Base
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
10.6: Working with pH
10.7: Acid and Base Equivalents
10.8: Some Common Acid-Base Reactions
10.9: Acidity and Basicity of Salt Solutions
10.10: Buffer Solutions
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10.1: Acids and Bases Definitions

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 hydrogen ions, H^+, in solution and a base produces hydroxide ions, 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; 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.

$$\mathrm{HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)} \tag{10.1.1}$$

In this reaction, hydrochloric acid (HCl) dissociates completely into hydrogen (H^+) and chloride (\Cl^{-}\)) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$\mathrm{HCl(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq)} \tag{10.1.2}$$

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:

$$\mathrm{NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)} \tag{10.1.3}$$

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

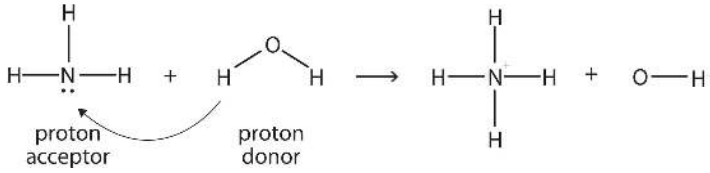
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

> *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:

$$\mathrm{NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)} \tag{10.1.4}$$

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:



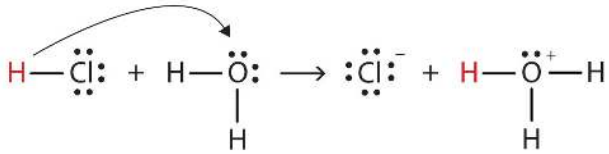
Because the water molecule *donates* a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which *accepts* the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

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.

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:

$$\mathrm{HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq)Cl^-(aq) + H_3O^+(aq)} \tag{10.1.5}$$

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; the 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.

Note: Acid and Base Definitions

- 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 10.1.1

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:

$$\mathrm{C_6H_5NH_2(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)}$$

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 10.1.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \tag{10.1.6}$$

Answer

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H_2O

? Exercise 10.1.2

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 HCl, H_3PO_4, NH_4^+ and $CH_3NH_3^+$ because they are Bronsted-Lowry acids. They all give away protons. In the case of HPO_4^{2-}, consider the following equation:

$$HPO_4^{2-}(aq) + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)$$

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:

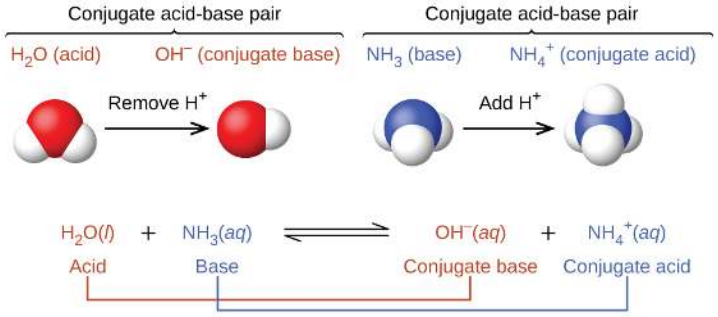
$$HPO_4^{2-}(aq) + H_2O(l) \rightarrow H_2PO_4^- + OH^-(aq)$$

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) 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, OH^-, and the conjugate acid of ammonia, NH_4^+:



In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.

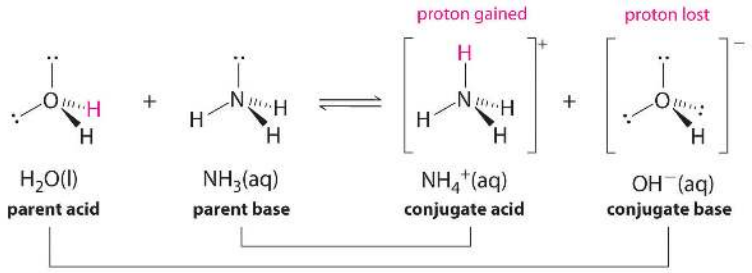


Figure 10.1.1. The pairing of parent acids and bases with conjugate acids and bases.

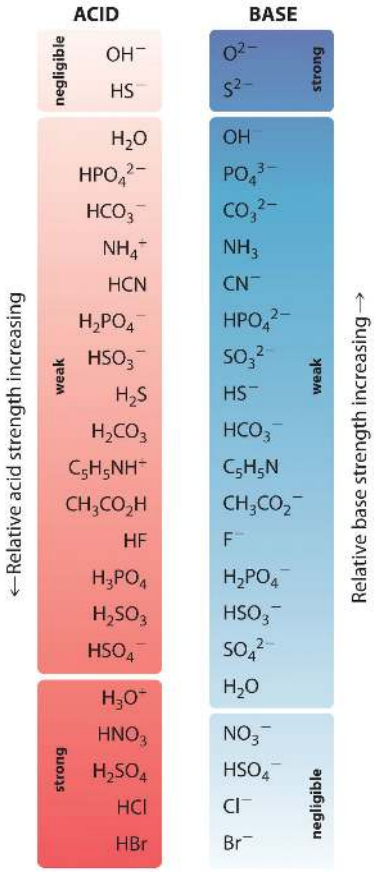


Figure 10.1.2: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Example 10.1.2

Identify the conjugate acid-base pairs in this equilibrium.

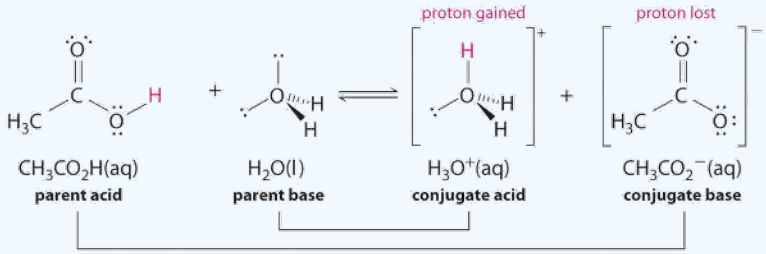
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

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, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 10.1.3

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 10.1.3

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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10.2: Acid and Base Strength

Learning Objectives

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.

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 $\mathrm{HCl(aq)}$. When HCl is dissolved in $\mathrm{H_2O}$, it completely **dissociates** (separates) into $\mathrm{H^+(aq)}$ and $\mathrm{Cl^-(aq)}$ ions; all the HCl molecules become ions:

$$\mathrm{HCl} \overset{100\,\%}{\rightarrow} \mathrm{H^+(aq) + Cl^-(aq)} \tag{10.2.1}$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $\mathrm{HC_2H_3O_2}$ is an example of a weak acid:

$$HC_2H_3O_2 \overset{\sim 5\%}{\longrightarrow} H^+(aq) + C_2H_3O_2^-(aq) \tag{10.2.2}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq) \tag{10.2.3}$$

As it turns out, there are very few strong acids, which are given in Table 10.2.1. 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.*

Figure 10.2.1: Some of the common strong acids and bases are listed here.

Strong Acids		Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

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 10.2.1); any base not listed is a weak base. All strong bases are $\mathrm{OH^-}$ compounds. So a base based on some other mechanism, such as $\mathrm{NH_3}$ (which does not contain $\mathrm{OH^-}$ ions as part of its formula), will be a weak base.

Example 10.2.1: Identifying Strong and Weak Acids and Bases

Identify each acid or base as strong or weak.

a. HCl
b. $\mathrm{Mg(OH)_2}$
c. $\mathrm{C_5H_5N}$

Solution

a. Because HCl is listed in Table 10.2.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 10.2.1, 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 10.2.1

Identify each acid or base as strong or weak.

a. $RbOH$
b. HNO_2

Answer

a. strong base
b. weak acid

Example 10.2.2: 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:

$$Ca(OH)_2 \rightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$$

Because $Ca(OH)_2$ is listed in Table 10.2.1, this reaction proceeds 100% to products.

Exercise 10.2.2

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:

$$HN_3 \rightarrow H^+(aq) + N_3^-(aq)$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Looking Closer: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for hydrochloric acid [$HCl(aq)$]. Vinegar has already been mentioned as a dilute solution of acetic acid [$HC_2H_3O_2(aq)$]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is ammonia (NH_3), which is found in numerous cleaning products. As we mentioned previously, ammonia is a base because it increases the hydroxide ion concentration by reacting with water:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq) \tag{10.2.4}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.



Figure 10.2.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for sodium hydroxide, although it is also used as a synonym for potassium hydroxide. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and form a clog in a pipe. Unfortunately, lye can also attack tissues and other substances in our bodies. Thus, when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners use peroxide compounds to react on the materials in the clog and clear the drain.

Chemical Equilibrium in Weak Acids and Bases

Ionization of weak acids or bases are reversible reactions, which means the forward and reverse reactions occur and eventually reach equilbrium. For example, the ionization of the weak acid $\mathrm{HC_2H_3O_2(aq)}$ is as follows:

$$\mathrm{HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)} \tag{10.2.5}$$

The reverse process also begins to occur:

$$\mathrm{H_3O^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) + H_2O(\ell)} \tag{10.2.6}$$

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:

$$\mathrm{HC_2H_3O_2(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)} \tag{10.2.7}$$

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 10.2.3: 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 10.2.3

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HF_{(aq)}$
b. $AgOH_{(aq)}$

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. $CH_3NH_2(aq) + H_2O(\ell) \leftrightarrows CH_3NH_3^+(aq) + OH^-(aq)$

Strengths of Conjugate Acid and Base Pairs

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure $10.2.2$).

The first six acids in Figure $10.2.2$ are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure $10.2.2$ form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and non-ionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure $10.2.2$ exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

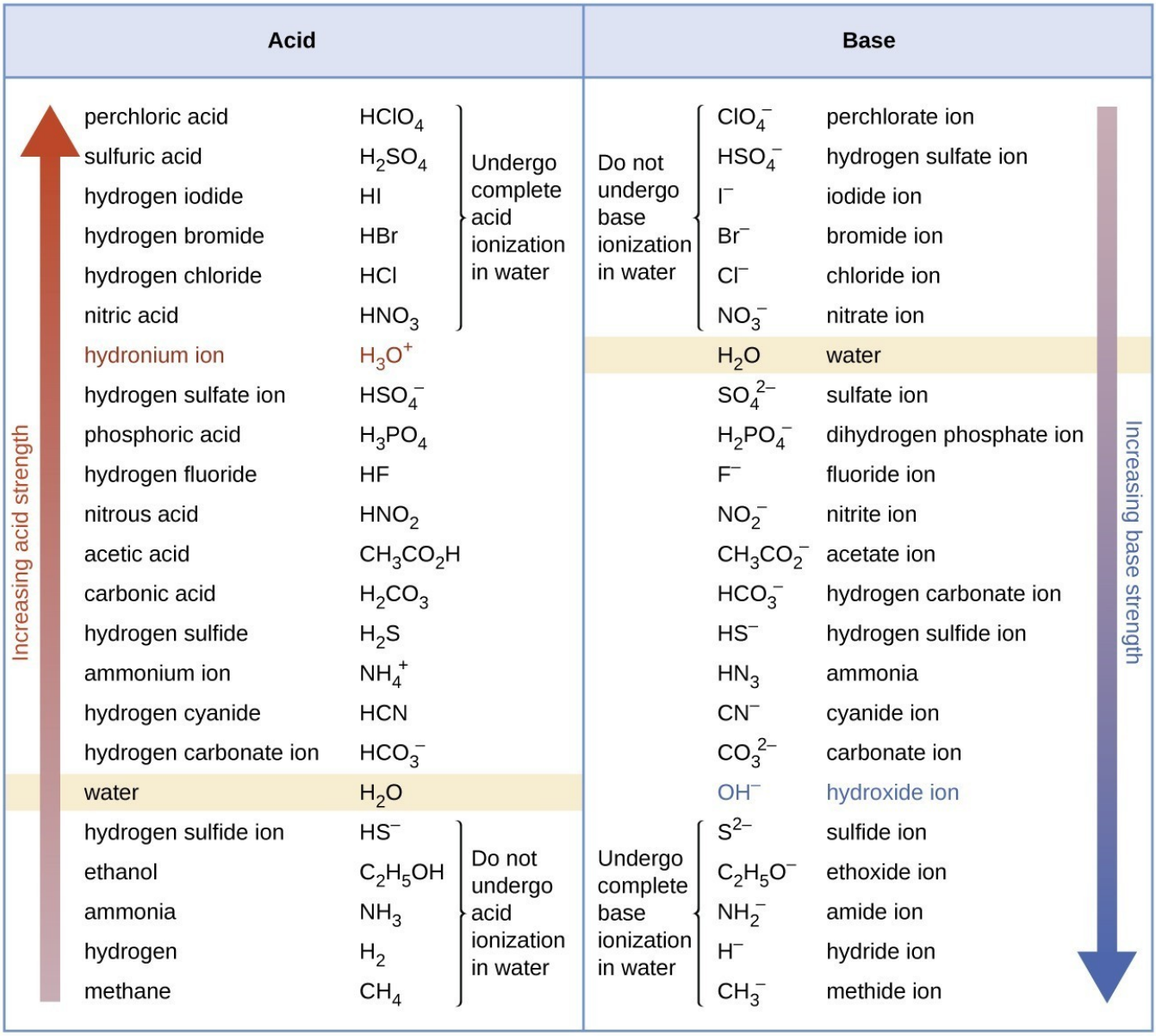


Figure 10.2.2: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 10.2.2 A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Key Takeaways

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.

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10.3: Acid Dissociation Constants

Learning Objectives

- Write the acid dissociation constant (K_a) expression.
- Determine the relative strength of an acid using the (K_a) value.

The ionization for a general weak acid, HA, can be written as follows:

$$\mathrm{HA}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{A^-}\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** ($\boldsymbol{K}_\mathrm{a}$) is the *equilibrium constant* for the ionization of an acid.

$$K_\mathrm{a} = \frac{\left[\mathrm{H^+}\right]\left[\mathrm{A^-}\right]}{[\mathrm{HA}]}$$

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 10.3.1: Acid Ionization Constants at $25^\circ\mathrm{C}$

Name of Acid	Ionization Equation	$\boldsymbol{K}_\mathrm{a}$
Sulfuric acid	$\mathrm{H_2SO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{HSO_4^-}$ $\mathrm{HSO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{SO_4^{2-}}$	very large 1.3×10^{-2}
Hydrofluoric acid	$\mathrm{HF} \rightleftharpoons \mathrm{H^+} + \mathrm{F^-}$	7.1×10^{-4}
Nitrous acid	$\mathrm{HNO_2} \rightleftharpoons \mathrm{H^+} + \mathrm{NO_2^-}$	4.5×10^{-4}
Benzoic acid	$\mathrm{C_6H_5COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{C_6H_5COO^-}$	6.5×10^{-5}
Acetic acid	$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{CH_3COO^-}$	1.8×10^{-5}
Carbonic acid	$\mathrm{H_2CO_3} \rightleftharpoons \mathrm{H^+} + \mathrm{HCO_3^-}$ $\mathrm{HCO_3^-} \rightleftharpoons \mathrm{H^+} + \mathrm{CO_3^{2-}}$	4.2×10^{-7} 4.8×10^{-11}

Hydrofluoric acid $HF_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

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10.4: Water as Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.
- Define and use the ion product constant for water, K_w, to calculate concentrations of H_3O^+ and OH^- in aqueous solutions.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$HCl + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{10.4.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion, a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{10.4.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{10.4.3}$$

This process is called the **autoionization of water** (Figure 10.4.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

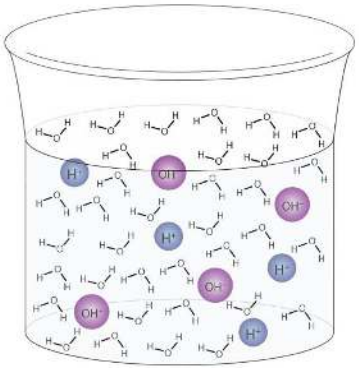


Figure 10.4.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

Example 10.4.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $OH^-(aq)$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

? Exercise 10.4.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Dissociation of Water

As we have already seen, H_2O can act as an acid or a base. 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:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{10.4.4}$$

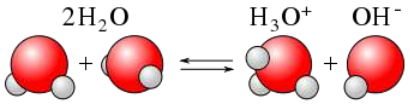


Figure 10.4.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{10.4.5}$$

We often use the simplified form of the reaction:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH-(aq)$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_w = [H^+][OH^-]$$

The **ion-product constant for water (K_w)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be *neutral*. To find the molarity of each ion, the square root of K_w is taken.

$$[H^+] = [OH^-] = 1.0\times10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[H^+]\times[OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of H^+ or $[H^+]$ is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- or $[OH^-]$ is greater than 1.0×10^{-7} M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This increases the concentration of H^+ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

$$HCl(g) \longrightarrow H^+(aq) + Cl^-(aq)$$

is forced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$

The increase in concentration of the OH^- ions will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, $[H^+]$ is greater than $[OH^-]$.
- For basic solutions, [OH−] is greater than $[H^+]$.
- For neutral solutions, $[H_3O^+] = [OH-] = 1.0\times10^{-7}$M

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$), you can calculate $[H^+]$. 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.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{10.4.6}$$

Example 10.4.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^{-3} M HCl?

Solution

Step 1: List the known values and plan the problem.

Known

- [HCl] = 2.0×10^{-3} M
- Kw = 1.0×10^{-14}

Unknown

- $[H^+]$=?M
- $[OH^-]$=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl− ion. The concentration of OH− can then be determined from the [H+] and Kw.

Step 2: Solve.

$$[H^+]=2.0\times10^{-3}\,M$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\,M$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

? Exercise 10.4.2

Sodium hydroxide (NaOH) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer

$[OH^-] = 0.001M$ or $1 \times 10^{-3}M$; $[H^+]=1\times10^{-11}M$.

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is H_2O acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some NH_4^+ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is H_2O acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

Answers

1. base
2. acid
3. acid
4. base

5. When water ionizes, equal amounts of H^+ (acid) and OH^- (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

[SIDE NOTE: It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.]

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10.5: Measuring Acidity in Aqueous Solutions- The pH Scale

Learning Objectives

- Define the pH scale and use it to describe acids and bases.
- Calculate the pH of a solution from $[H_3O^+]$ and $[OH^-]$.

Knowing the amount of acid and base in solutions is extremely important for a wide variety of applications ranging from brewing beer or wine to studying the effects of ocean acidification to health and medicine. Scientists are good at calculating and measuring the concentration of hydronium in a solution, however, there is a more convenient way to make comparisons between solutions – *the pH scale*.

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure $10.5.1$ 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.

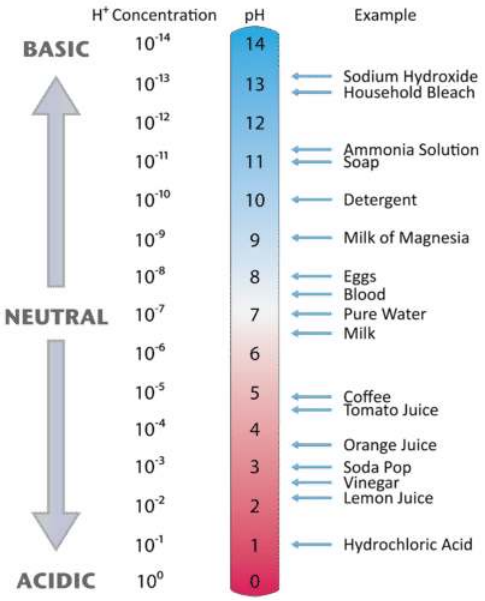


Figure 10.5.1: The relationship between [H+] and *pH values for several common materials.*

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in Table \(\PageIndex{1}.

Table 10.5.1: Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	pH < 7

Classification	Relative Ion Concentrations	pH at 25°C
neutral	$[H^+] = [OH^-]$	pH = 7
acidic	$[H^+] > [OH^-]$	pH < 7
basic	$[H^+] < [OH^-]$	pH > 7

Example 10.5.1

Find the pH, given the $[H^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

pH = - log $[H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. pH = - log $[1 \times 10^{-3}]$ = 3.0 (1 decimal place since 1 has 1 significant figure)
b. pH = - log $[2.5 \times 10^{-11}]$ = 10.60 (2 decimal places since 2.5 has 2 significant figures)
c. pH = - log $[4.7 \times 10^{-9}]$ = 8.33 (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

Exercise 10.5.1

Find the pH, given $[H^+]$ of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7} M

Answer

a. 3.24

b. 7.00

Figure 10.5.2 lists the pH of several common solutions. The most *acid*ic among the listed solutions is 1 M HCl with the lowest pH value (0.0): battery acid is the next most acidic solution with a pH value of 0.3. The most *basic* is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

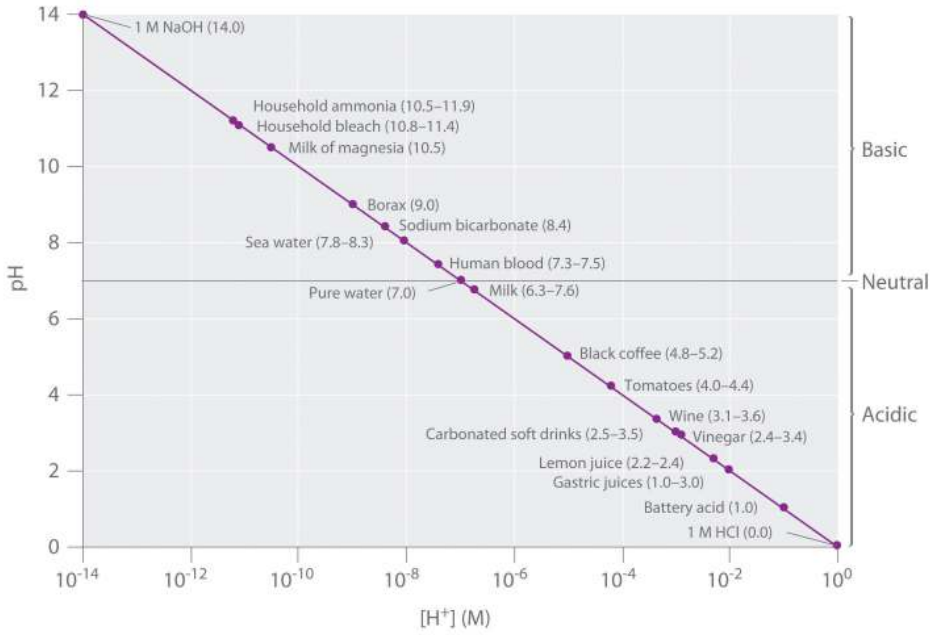


Figure 10.5.2: A Plot of pH versus [H^+] for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

Example 10.5.2

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

Solution

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 10.5.2

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. slightly basic

b. basic

c. acidic

Measuring pH

Tools have been developed that make the measurement of pH simple and convenient. For example, pH paper (Figure 10.5.3) consists of strips of paper impregnated with one or more **acid-base indicators**, which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH

paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the H^+ ion concentration (Figure 10.5.3).



Figure 10.5.3: Ways to measure pH. (left) These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center strip is pH range 5-10 and shows results of a 6.97 buffer solution sample; the strip on the right measures a broad range (pH 1-14) and shows results of a 10% bleach water solution sample. This image can be enlarged by clicking on it. (right) These three meters and probes can measure pH (left) and electrical conductivity (center and right). Photos by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).

Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq) \tag{10.5.1}$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{10.5.2}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq) \tag{10.5.3}$$

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \tag{10.5.4}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes

uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 10.5.4). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

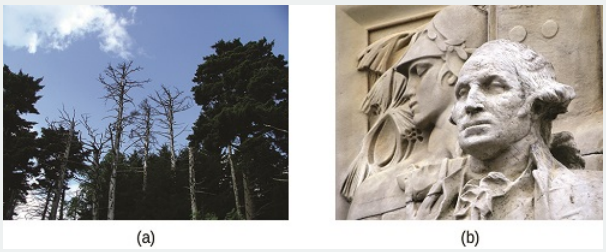


Figure 10.5.4: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

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10.6: Working with pH

Learning Objectives

- Calculate pH from $[H_3O^+]$ and $[H_3O^+]$ from pH.

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?

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned} \tag{10.6.1}$$

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.

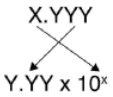
Example 10.6.2: Converting Ph to Hydronium Concentration

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

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: a. $[H_3O^+]$ =1 × 10^{-3} M b. $[H_3O^+]$ =2.5 ×10^{-11} M c. $[H_3O^+]$ = 4.7 ×10^{-9} M Find: ? pH
Plan the problem.	Need to use the expression for pH (Equation ???). pH = - log $[H_3O^+]$

Steps for Problem Solving	
Calculate.	Now substitute the known quantity into the equation and solve. a. pH = - log [1 × 10^{-3}] = 3.0 (1 decimal places since 1 has 1 significant figure) b. pH = - log [2.5 ×10^{-11}] = 10.60 (2 decimal places since 2.5 has 2 significant figures) c. pH = - log [4.7 ×10^{-9}] = 8.30 (2 decimal places since 4.7 has 2 significant figures) 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: 

? Exercise 10.6.2

Find the pH, given [H_3O^+] of the following:

a. 5.8 ×10^{-4} M
b. 1.0×10^{-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 ??? for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[\mathrm{H_3O^+}] = \mathrm{antilog}(-pH) \tag{10.6.2}$$

or

$$[\mathrm{H_3O^+}] = 10^{-pH} \tag{10.6.3}$$

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 **5.0 × 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 **5.0×10^{-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 10.6.3: 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

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH = 12.6 Find: $[H_3O^+]$ = ? M
Plan the problem.	Need to use the expression for $[H_3O^+]$ (Equation 10.6.3). $[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$
Calculate.	Now substitute the known quantity into the equation and solve. $[H_3O^+]$ = antilog (12.60) = 2.5×10^{-13} M (2 significant figures since 4.7 has 12.60 2 decimal places) or $[H_3O^+] = 10^{-12.60} = 2.5 \times 10^{-13}$ M (2 significant figures since 4.7 has 12.60 2 decimal places) 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: X.YYY Y.YY x 10^x

Exercise 10.6.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

Answer

1.5×10^{-8} M

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10.7: Acid and Base Equivalents



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10.8: Some Common Acid-Base Reactions



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10.9: Acidity and Basicity of Salt Solutions

Learning Objectives

- Identify a salt solution as acidic, basic, or neutral.

A salt is an ionic compound that is formed when an acid and a base neutralize each other. While it may seem that salt solutions are always neutral, they can frequently be either acidic or basic.

Consider the salt formed when the weak acid hydrofluoric acid is neutralized by the strong base sodium hydroxide. The molecular and net ionic equations are shown below.

$$\mathrm{HF}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaF}\,(aq) + \mathrm{H_2O}\,(l)$$
$$\mathrm{HF}\,(aq) + \mathrm{OH^-}\,(aq) \rightarrow \mathrm{F^-}\,(aq) + \mathrm{H_2O}\,(l)$$

Since sodium fluoride is soluble, the sodium ion is a spectator ion in the neutralization reaction. The fluoride ion is capable of reacting, to a small extent, with water, accepting a proton.

$$\mathrm{F^-}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{HF}\,(aq) + \mathrm{OH^-}\,(aq)$$

The fluoride ion is acting as a weak Brønsted-Lowry base. The hydroxide ion that is produced as a result of the above reaction makes the solution slightly basic. **Salt hydrolysis** is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.

Salts That Form Basic Solutions

When solid sodium fluoride is dissolved into water, it completely dissociates into sodium ions and fluoride ions. The sodium ions do not have any capability of hydrolyzing, but the fluoride ions hydrolyze to produce a small amount of hydrofluoric acid and hydroxide ion.

$$\mathrm{F^-}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{HF}\,(aq) + \mathrm{OH^-}\,(aq)$$

Salts that are derived from the neutralization of a weak acid (HF) by a strong base (NaOH) will always produce salt solutions that are basic.

Salts That Form Acidic Solutions

Ammonium chloride $(\mathrm{NH_4Cl})$ is a salt that is formed when the strong acid HCl is neutralized by the weak base $\mathrm{NH_3}$. Ammonium chloride is soluble in water. The chloride ion produced is incapable of hydrolyzing because it is the conjugate base of the strong acid HCl. In other words, the $\mathrm{Cl^-}$ ion cannot accept a proton from water to form HCl and $\mathrm{OH^-}$, as the fluoride ion did in the previous section. However, the ammonium ion is capable of reacting slightly with water, donating a proton and so acting as an acid.

$$\mathrm{NH_4^+}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H_3O^+}\,(aq) + \mathrm{NH_3}\,(aq)$$

Salts That Form Neutral Solutions

A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7. An example is sodium chloride, formed from the neutralization of HCl by NaOH. A solution of NaCl in water has no acidic or basic properties, since neither ion is capable of hydrolyzing. Other salts that form neutral solutions include potassium nitrate $(\mathrm{KNO_3})$ and lithium bromide (LiBr). The table below summarizes how to determine the acidity or basicity of a salt solution.

Table 10.9.1

Salt formed from:	Salt Solution
Strong acid + Strong base	Neutral
Strong acid + Weak base	Acidic
Weak acid + Strong base	Basic

Salts formed from the reaction of a weak acid and a weak base are more difficult to analyze due to competing hydrolysis reactions between the cation and the anion. These salts are not considered in this chapter's concept.

Summary

- Salt hydrolysis is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.
- Salts that are derived from the neutralization of a weak acid by a strong base will always produce salt solutions that are basic.
- Salts that are derived from the neutralization of a strong acid by a weak base will always produce salt solutions that are acidic.
- A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7.

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10.10: 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 10.10.1). 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 ($NH_4Cl(aq)$).

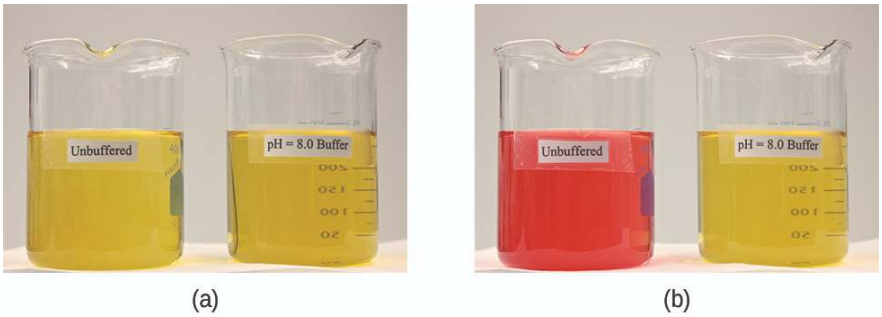


Figure 10.10.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably 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 10.10.2).

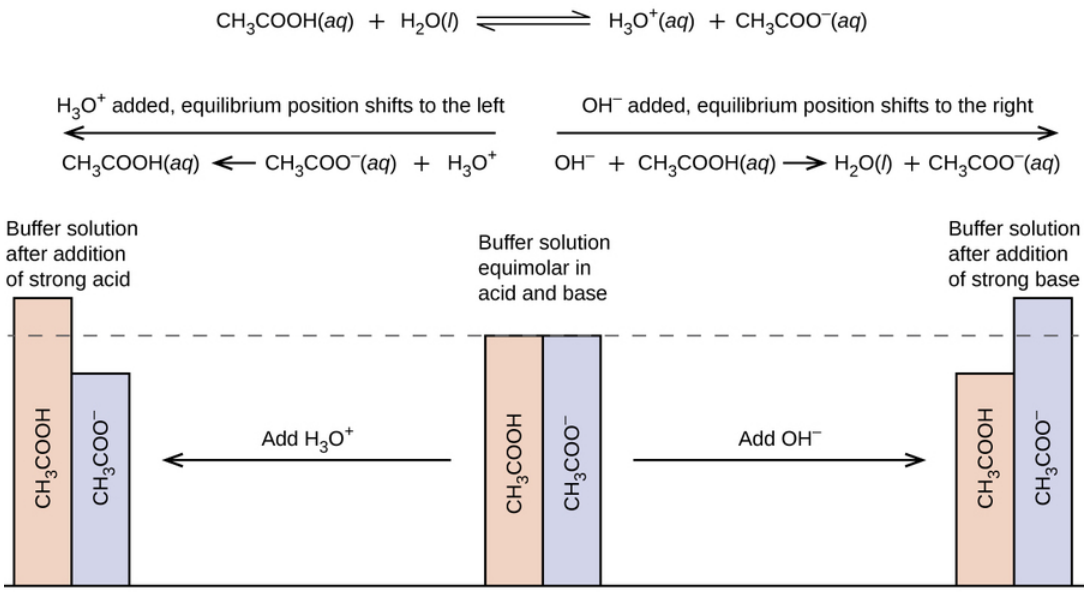


Figure 10.10.2: This diagram shows the buffer action of these reactions.

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:

$$\mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l)$$

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:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l)$$

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 10.10.1: pH Changes in Buffered and Unbuffered Solutions

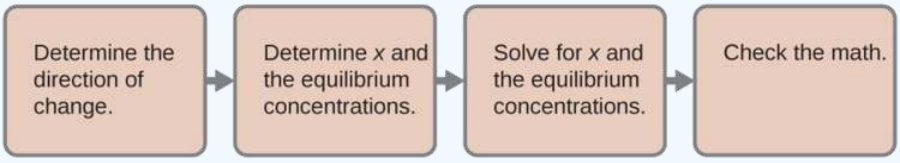
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

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 $\mathrm{H_3O^+}$, $\mathrm{CH_3CO_2^-}$, and $\mathrm{CH_3CO_2H}$ is:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

The equilibrium constant for $\mathrm{CH_3CO_2H}$ is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[\mathrm{CH_3CO_2H}] = [\mathrm{CH_3CO_2^-}] = 0.10\ M$ and $[\mathrm{H_3O^+}] = \sim 0\ M$, the reaction shifts to the right to form $\mathrm{H_3O^+}$.

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:

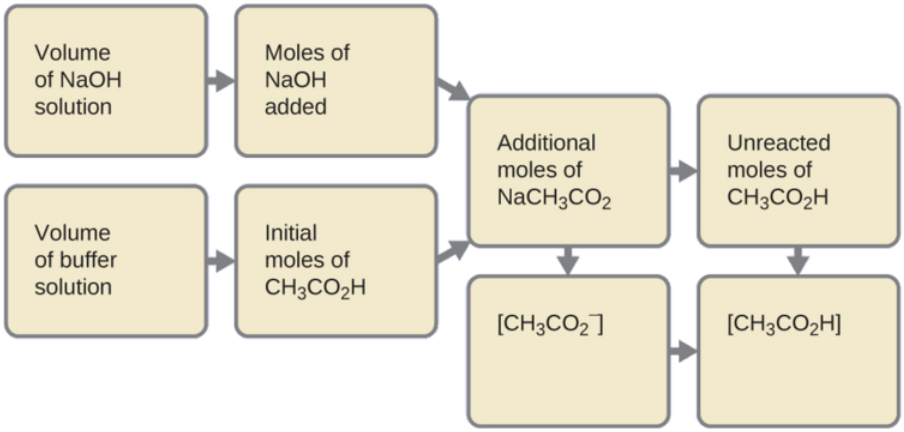
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

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 1.0×10^{-4} mol of NaOH neutralizes 1.0×10^{-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 1.0×10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

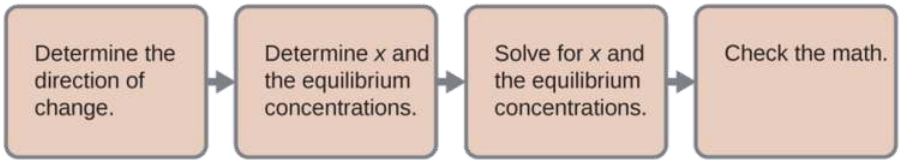
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \nonumber \]

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 1.8×10^{-5}-*M* solution of HCl). The volume of the final solution is 101 mL.

Solution

This 1.8×10^{-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 1.0×10^{-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 10.10.1

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a 1.8×10^{-5} *M* HCl solution from 4.74 to 3.00.

Answer

Initial pH of 1.8×10^{-5} *M* HCl; pH = −log[H_3O^+] = −log[1.8×10^{-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 = 1.0×10^{-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 10.10.3). 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 10.10.3: 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 10.10.4shows 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.

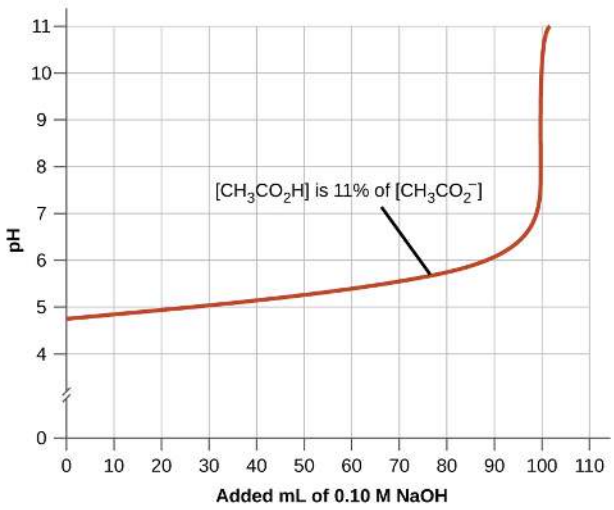


Figure 10.10.4: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2^-] = 0.10\ M$.

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:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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, $\mathrm{H_2CO_3}$ is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathrm{HCO_3^-}$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the $\mathrm{H_2CO_3}$ concentration is significantly lower than that of the $\mathrm{HCO_3^-}$ 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 $\mathrm{HCO_3^-}$ ion, producing $\mathrm{H_2CO_3}$. 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 $\mathrm{CO_2}$ from the blood through the lungs driving the equilibrium reaction such that $[\mathrm{H_3O^+}]$ is lowered. If the blood is too alkaline, a lower breath rate increases $\mathrm{CO_2}$ concentration in the blood, driving the equilibrium reaction the other way, increasing $[\mathrm{H^+}]$ 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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10.11: Titration

Learning Objectives

- Describe a titration experiment.
- Explain what an indicator does.
- 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 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.

In a titration, one reagent has a known concentration or amount, while the other reagent has an unknown concentration or amount. Typically, the known reagent (the **titrant**) is added to the unknown quantity and is dissolved in solution. The unknown amount of substance (the **analyte**) may or may not be dissolved in solution (but usually is). The titrant is added to the analyte using a precisely calibrated volumetric delivery tube called a burette (also spelled buret; see Figure 10.11.1). The burette has markings to determine how much volume of solution has been added to the analyte. When the reaction is complete, it is said to be at the **equivalence point**; the number of moles of titrant can be calculated from the concentration and the volume, and the balanced chemical equation can be used to determine the number of moles (and then concentration or mass) of the unknown reactant.



Figure 10.11.1 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:

$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

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 10.11.1

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:

$$2\text{HNO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Ca(NO}_3\text{)}_2 + 2\text{H}_2\text{O}$$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

$$\text{\# moles HNO}_3 = (0.04402\ \text{L})(0.0885\ \text{M}) = 0.00390\ \text{mol HNO}_3$$

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 10.11.1

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:

$$\mathrm{H_2C_2O_4 + 2\,NaOH \rightarrow Na_2C_2O_4 + 2\,H_2O}$$

Answer

0.182 g

How does one know if a reaction is at its equivalence point? Usually, the person performing the titration adds a small amount of an **indicator**, a substance that changes color depending on the acidity or basicity of the solution. Because different indicators change colors at different levels of acidity, choosing the correct one is important in performing an accurate titration.

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CHAPTER OVERVIEW

12: Introduction to Organic Chemistry - Alkanes

12.1: The Nature of Organic Molecules
12.2: Families of Organic Molecules - Functional Groups
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
12.4: Drawing Organic Structures
12.5: The Shapes of Organic Molecules
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12.10: Drawing and Naming Cycloalkanes

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12.1: The Nature of Organic Molecules

Learning Objectives

- Describe the basic structural properties of simple organic molecules.

Organic chemistry is the study of the chemistry of carbon-containing compounds. Carbon is singled out because it has a chemical diversity unrivaled by any other chemical element. Its diversity is based on the following:

- Carbon atoms bond reasonably strongly with other carbon atoms.
- Carbon atoms bond reasonably strongly with atoms of other elements.
- Carbon atoms make a large number of covalent bonds (four).

Curiously, elemental carbon is not particularly abundant. It does not even appear in the list of the most common elements in Earth's crust. Nevertheless, all living things consist of organic compounds. Most organic chemicals are covalent compounds, which is why we introduce organic chemistry here. By convention, compounds containing carbonate ions and bicarbonate ions, as well as carbon dioxide and carbon monoxide, are not considered part of organic chemistry, even though they contain carbon.

Structural Properties of Carbon Compounds

A carbon atom has four valence electrons, it is **tetravalent**. Carbon can form four *covalent* bonds, or *share electrons with* up to four atoms in order to gain a complete octet. The simplest carbon compounds contain only carbon and hydrogen and are called **hydrocarbons**. Methane, the simplest hydrocarbon, contains a single carbon with four covalently bonded hydrogen atoms. Recalling what you have learned about molecular structures and VSEPR, we know that methane is **tetrahedral** (four electron groups and no lone pairs).

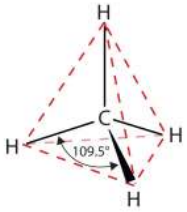


Figure 12.1.1: The Tetrahedral Methane Molecule

Carbon can also form **double bonds** by sharing *four electrons* with a neighboring carbon atom or **triple bonds** by sharing *six electrons* with a neighboring carbon atom. As shown in Figure 12.1.2 below, carbon with three electron groups attached will be **trigonal planar**, and carbon with two electron groups attached will be **linear**.

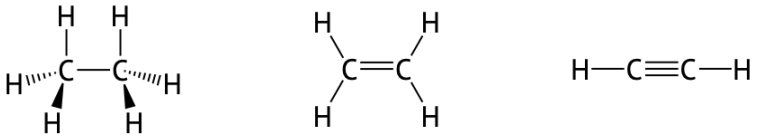


Figure 12.1.2: Two carbons can be attached together in single bond, a double bond, or a triple bond. Notice, in each example carbon makes four total bonds. The number of hydrogen atoms in each molecule decreases as the number of carbon–carbon bonds increase.

Simple hydrocarbon compounds are *nonpolar* due to the shape and the small electronegativity difference between carbon and hydrogen atoms. When carbon is bonded to a halogen or oxygen atom, the resulting bond is *polar*. It may be useful to review the section on electronegativity and polarity of bonds and molecules to be able to describe the properties of different organic compounds, specifically how they react and interact with other molecules.

Comparing Organic and Inorganic Compounds

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 12.1.1. Keep in mind, however, that there are exceptions to every category in this table.

Table 12.1.1: Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic Properties	**Example:** Hexane	**Inorganic Properties**	**Example:** NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

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12.2: Families of Organic Molecules - Functional Groups

Learning Objectives

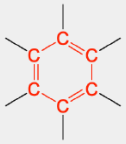
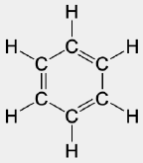
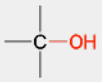
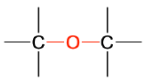
- Identify and describe functional groups in organic molecules.

Organic molecules can be classified into *families* based on structural similarities. Within a family, molecules have similar physical behavior and often have predictable chemical reactivity. The structural components differentiating different organic families involve specific arrangements of atoms or bonds, called **functional groups**. If you understand the behavior of a particular functional group, you can describe the general properties of that class of compounds.

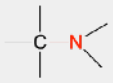
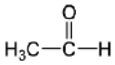
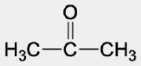
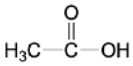
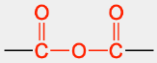
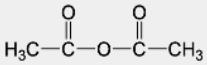
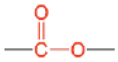
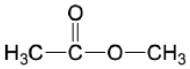
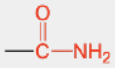
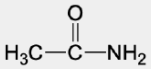
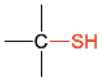
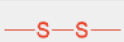
The simplest organic compounds are in the **alkane** family and contain only carbon–carbon and carbon–hydrogen *single* bonds but do not have any specific functional group. Hydrocarbons containing at least one carbon–carbon double bond, (denoted C=C), are in the **alkene** family. **Alkynes** have at least one carbon–carbon triple bond (C≡C). Both carbon–carbon double bonds and triple bonds chemically react in specific ways that differ from reactions of alkanes and each other, making these specific functional groups.

In the next few chapters, we will learn more about additional functional groups that are made up of atoms or groups of atoms attached to hydrocarbons. Being able to recognize different functional groups will help to understand and describe common medications and biomolecules such as amino acids, carbohydrates, and fats. Table 12.2.1 and Figure 12.2.1 below list several of the functional groups to become familiar with as you learn about organic chemistry.

Table 12.2.1: Organic Families and Functional Groups

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name	Name Suffix
alkane	none	$CH_3CH_2CH_3$	propane	*-ane*
alkene		$H_2C=CH_2$	ethene (ethylene)	*-ene*
alkyne		HC≡CH	ethyne (acetylene)	*-yne*
aromatic			benzene	none
alkyl halide	 (X = F, Cl, Br, I)	CH_3CH_2Cl	chloroethane	none
alcohol		CH_3CH_2OH	ethanol	*-ol*
ether		$CH_3CH_2–O–CH_2CH_3$	diethyl ether	none*

Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hydrogens).
*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name	Name Suffix
amine		$CH_3CH_2NH_2$	ethylamine	*-amine*
aldehyde			ethanal	*-al*
ketone			propanone (acetone)	*-one*
carboxylic acid			ethanoic acid (acetic acid)	*-oic acid*
anhydride			acetic anhydride	none
ester			methyl ethanoate (methyl acetate)	*-ate*
amide			acetamide	*-amide*
thiol		CH_3CH_2SH	ethanethiol	*-thiol*
disulfide		$CH_3S–SCH_3$	dimethyl disulfide	none
sulfide		$CH_3CH_2SCH_3$	ethyl methyl sulfide	none

Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hydrogens).
*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

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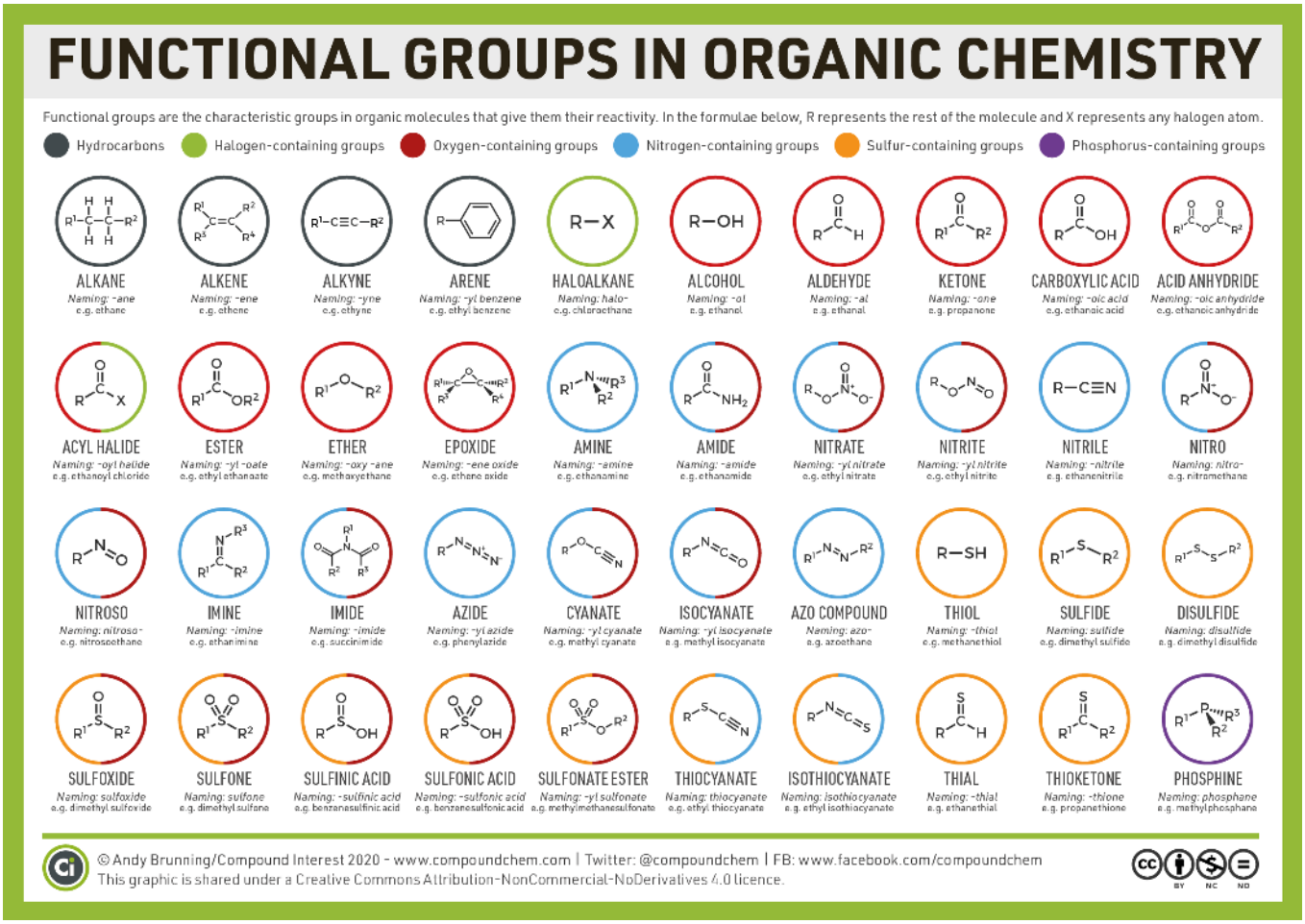


Figure 12.2.1: Functional groups in organic chemistry. (CC BY-NC-ND, CompoundChem.com).

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12.3: The Structure of Organic Molecules - Alkanes and Their Isomers

Learning Objectives

- To identify simple alkanes as straight-chain or branched-chain.
- Describe and recognize structural and functional group isomers.

As you just learned, there is a wide variety of organic compounds containing different functional groups. However, all organic compounds are hydrocarbons, they contain hydrogen and carbon. The general rule for hydrocarbons is that any carbon must be bonded to at least one other carbon atom, except in the case of methane which only contains one carbon. The bonded carbons form the *backbone* of the molecule to which the hydrogen atoms (or other functional groups) are attached.

Hydrocarbons with only carbon-to-carbon single bonds (C–C) are called **alkanes** (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in these molecules.

> Saturated fats and oils are organic molecules that do not have carbon-to-carbon double bonds (C=C).

The three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) shown in Figure 12.3.1, are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit (called methylene). Alkanes follow the general formula: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

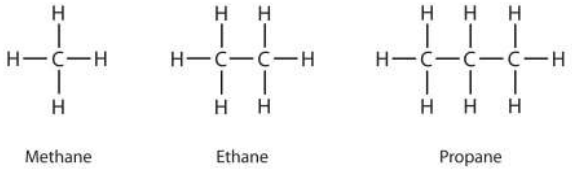
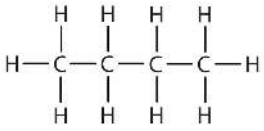


Figure 12.3.1: The Three Simplest Alkanes

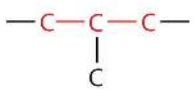
Isomers

Alkanes that contain one continuous chain of linked carbons are called **straight-chain** alkanes. As the number of carbons in a chain increases beyond three, the arrangement of atoms can expand to include **branched-chain** alkanes. In a branched chain, one or more hydrogen atoms along the chain is replaced by a carbon atom (or a separate chain of carbon atoms). It is important to note that while the structural arrangement of these chains are different, continuous versus branched, they both still follow the same general formula for alkanes as introduced above, C_nH_{2n+2}. In fact, alkane chains that have the same molecular formula (same number of carbon and hydrogen), but a different arrangement of atoms, are called **isomers**. Let's look at an example below:

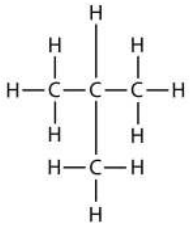
The structure of butane (C_4H_{10}) is written by stringing four carbon atoms in a row, and then adding enough hydrogen atoms to give each carbon atom four bonds:



Butane is a straight-chain alkane, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then *branch* the fourth carbon off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds:



The result is the isomer 2-methylpropane (also called isobutane), which is a branched-chain alkane with the same formula as butane, (C_4H_{10}). However, it is a *different* molecule with a *different* name and *different* chemical properties. A side-by-side comparison of these two molecules is shown in the below figure.

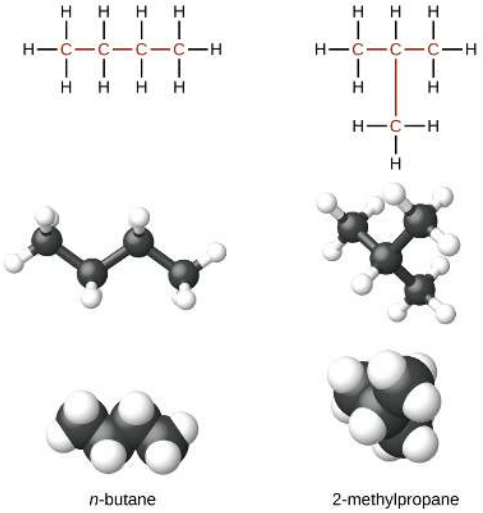


Figure 12.3.1: n-butane and 2-methylpropane. The compounds *n*-butane and 2-methylpropane are structural isomers, meaning they have the same molecular formula, C_4H_{10}, but different spatial arrangements of the atoms in their molecules. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching.

The four-carbon straight chain butane may be drawn with different bends or kinks in the backbone (Figure 12.3.2) because the groups can rotate freely about the C–C bonds. This rotation or bending of the carbon chain does *not* change the identity of the compound; all of the following structures represent the *same* compound, butane, with different bends in the chain:

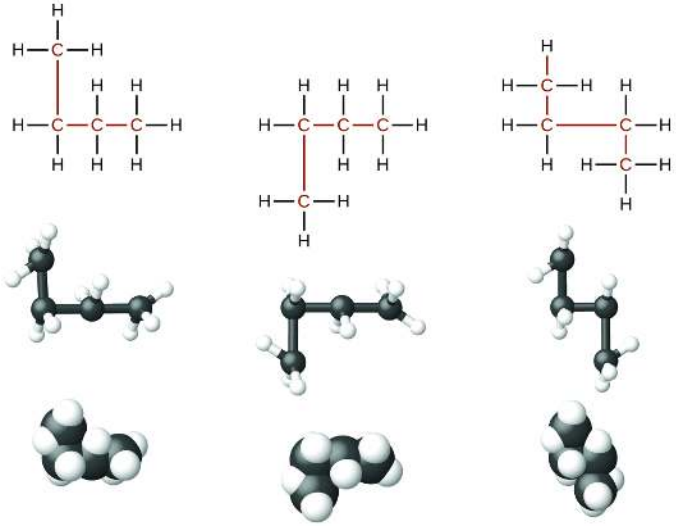
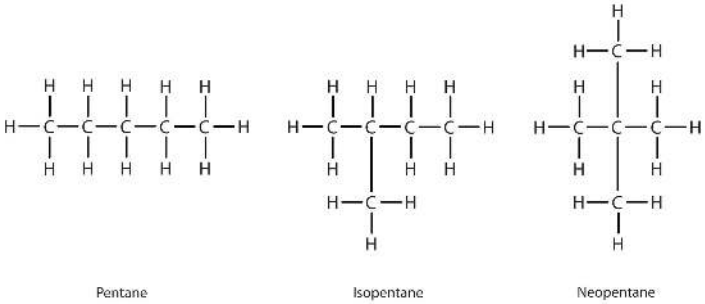


Figure 12.3.2: These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

When identifying isomers, it is useful to trace the carbon backbone with your finger or a pencil and count carbons until you need to lift your hand or pencil to get the another carbon. Try this with each of the above arrangements of four carbons, then do the same

with 2-methylpropane. Butane has a continuous chain of four carbons no matter how the bonds are rotated – you can connect the carbons in a line without lifting your finger from the page. How many continuous carbons are in the 2-methylpropane backbone? You should be able to count a continuous chain of three carbon atoms only, with the fourth carbon attached as a branch, (compare the two structures in Figure 12.3.1). In a later chapter, you will learn how to systematically name compounds by counting the number of carbons in the longest continuous chain and identifying any functional groups present.

Adding one more carbon to the butane chain gives pentane, which has the formula, C_5H_{12}. Pentane and its two branched-chain isomers are shown below. The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C. The names isopentane and neopentane are common names for these molecules. As mentioned above, we will learn the systematic rules for naming compounds in later chapters.



A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

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12.4: Drawing Organic Structures

Learning Objectives

- Draw condensed structures and line structures for simple compounds from the given molecular formulas.
- Convert between expanded, condensed and line structures.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the number and type of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and 2-methylpropane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them (**expanded structure**). This type of structure allows for easy identification of specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas that show the bonds between *all* atoms are sometimes difficult to type/write and take up a lot of space, especially when the number of atoms greatly increases. Chemists often use **condensed structures**, that show hydrogen atoms right next to the carbon atoms to which they are attached, to alleviate these problems. The ultimate condensed formula is a **line (or line-angle) structure**, in which carbon atoms are implied at the corners and ends of lines rather than written out, and each carbon atom is understood to be attached to the appropriate amount of hydrogen atoms to give each carbon atom four bonds. Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom. All three of these structure types are illustrated for butane and its isomer, 2-methylpropane in Figure 12.4.1 below.

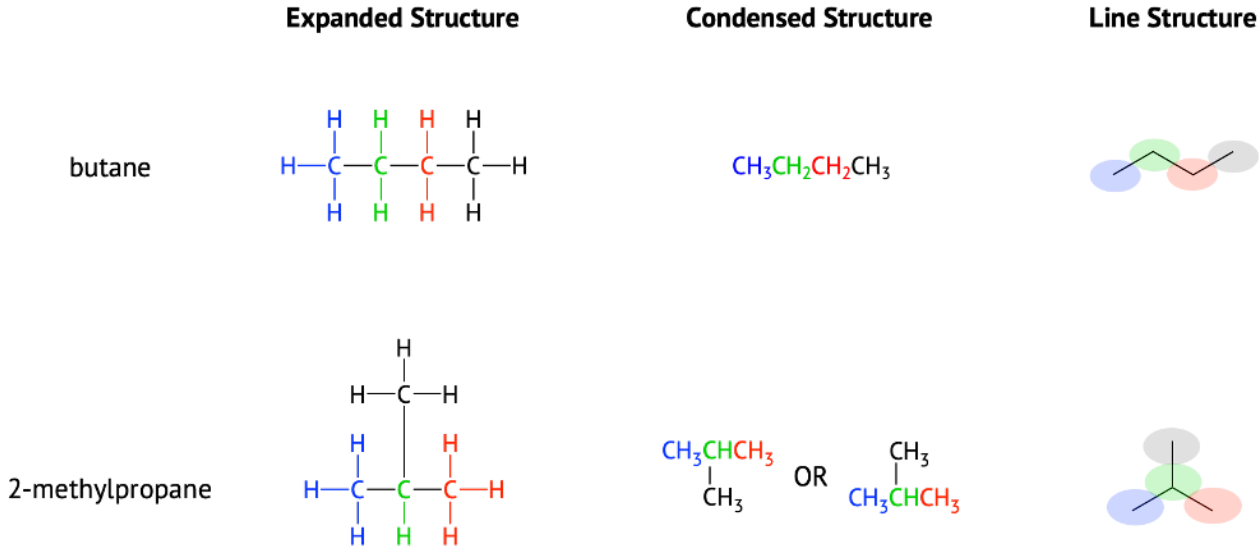


Figure 12.4.1: Structural representations for butane and its isomer, 2-methylpropane. (The colors are used to help identify carbons and do not represent any special properties.)

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12.5: The Shapes of Organic Molecules



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12.6: Naming Alkanes

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases: there are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes, etc. It would be difficult to assign each compound unique individual names that we could remember easily. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names mentioned earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.)

In the IUPAC system, a compound is named according to the number of carbons in the longest continuous chain (LCC) or parent chain and the family it belongs to. Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by a numerical prefix at the beginning of the name:

Prefix (substituent) – Parent (# carbons) – Suffix (family name)

2-methylpropane

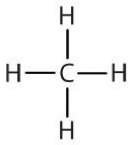
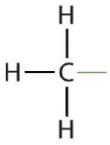
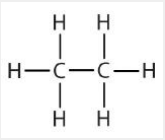
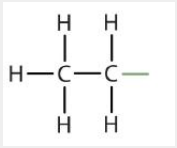
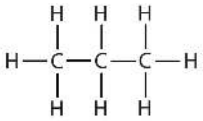
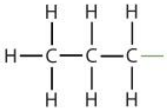
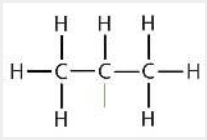
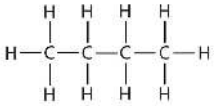
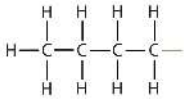
(Table 12.6.1) below lists the IUPAC parent names that are used for charbon chains containing 1 to 10 carbons, along with straight-chain alkane examples for each. Notice that the suffix for each example in this table is *-ane*, which indicates these are members of the alk*ane* family.

Table 12.6.1: Parent name for 1-10 carbons and Example Alkanes

Number of Carbons	Parent Chain (LCC) Name	Example Alkane Name	Example Condensed Structural Formula
1	*meth-*	methane	CH_4
2	*eth-*	ethane	CH_3CH_3
3	*prop-*	propane	$CH_3CH_2CH_3$
4	*but-*	butane	$CH_3CH_2CH_2CH_3$
5	*pent-*	pentane	$CH_3CH_2CH_2CH_2CH_3$
6	*hex-*	hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	*hept-*	heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	*oct-*	octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	*non-*	nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	*dec-*	decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Atoms or groups of atoms that branch off the parent chain are called **substituents**. When the substituent is a carbon or group of carbons, such as $–CH_3$ or $–CH_2CH_3$, it is called an **alkyl group**. Alkyl groups are alkanes that have had one hydrogen removed to allow for binding to a main chain carbon and are named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the $–CH_3$ group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a **methyl group**. Removing a hydrogen from ethane, CH_3CH_3, gives $–CH_2CH_3$, or the **ethyl group**. The alkyl groups we will use most frequently are listed in Table 12.6.2 Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 12.6.2: Common Alkyl Groups

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		$CH_3–$
ethane		ethyl		$CH_3CH_2–$
propane		propyl		$CH_3CH_2CH_2–$
		isopropyl		$(CH_3)_2CH–$
butane		butyl		$CH_3CH_2CH_2CH_2–$
		sec-butyl		
		isobutyl		
		tert-butyl (tBu)		

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 12.6.1).

Step 1: **Name the parent chain.** Find the longest continuous chain, (it may not always be the most obvious chain written in one line), and name according to the number of carbon atoms it contains. Add the suffix *-ane* to indicate that the molecule is an alkane. Use Table 12.6.1 as a reference to start, but it is a good idea to commit these to memory.

Step 2: **Number the carbon atoms in the parent chain,** giving carbons with any substituents attached the lowest number possible. These numbers are used to locate where substituents are attached to a main chain.

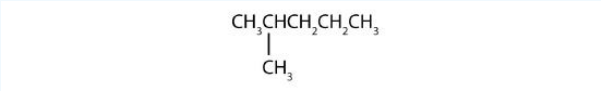
Step 3: **Name any substituents (including the location number).** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

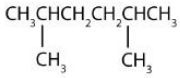
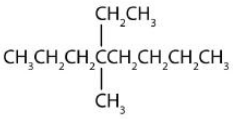
Step 4: **Write the name of the compound as a single word placing the substituent groups first (in alphabetical order), then the parent name, then the family name.** Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to practice it, not just memorize the rules. It's easier than it looks.

Example 12.6.1

Name each compound.

1. 

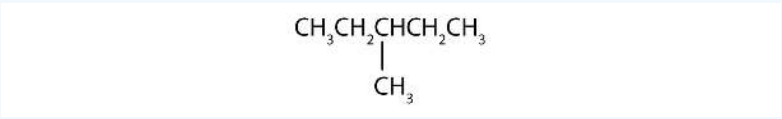
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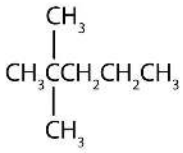
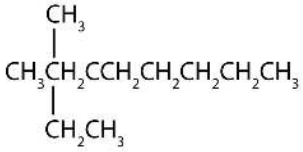
Solution

1. Step 1: The LCC has five carbon atoms, and so the parent compound name is pentane. Step 2: Number the carbons in the LCC from left to right. Step 3: There is a methyl group attached to carbon #2 of the pentane chain. Step 4: The name is 2-methylpentane.
2. Step 1: The LCC has six carbon atoms, so the parent compound is hexane. Step 2: Number the carbons in the LCC from left to right (or right to left, either way will be identical numbering). Step 3: There are two methyl groups attached to the second and fifth carbon atoms. Step 4: The name is 2,5-dimethylhexane.
3. Step 1: The LCC has eight carbon atoms, so the parent compound is octane. Step 2: Number the carbons in the LCC from left to right to give the *lower* number. Step 3: There are methyl and ethyl groups, both attached to the fourth carbon atom. Step 4: The correct name is thus 4-ethyl-4-methyloctane.

Exercise 12.6.1

Name each compound.

1. 

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- 

Example 12.6.2

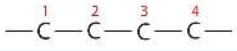
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

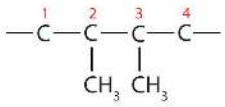
Solution

In drawing structures, always start with the parent chain.

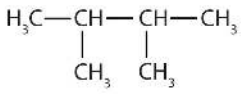
a. The parent chain is butane, indicating four carbon atoms in the LCC.



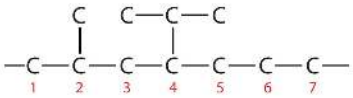
Then add the substituents at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl ($-CH_3$) groups, one on the second carbon atom and one on the third.



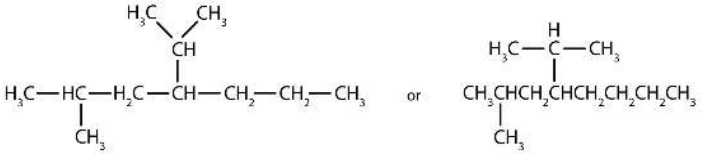
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds total.



- Adding the substituents at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas (both are correct):



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

? Exercise 12.6.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

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12.7: Properties of Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table 12.7.1 describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H_2O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table 12.7.1: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH_4	–182	–164	0.668 g/L	gas
ethane	C_2H_6	–183	–89	1.265 g/L	gas
propane	C_3H_8	–190	–42	1.867 g/L	gas
butane	C_4H_{10}	–138	–1	2.493 g/L	gas
pentane	C_5H_{12}	–130	36	0.626 g/mL	liquid
hexane	C_6H_{14}	–95	69	0.659 g/mL	liquid
octane	C_8H_{18}	–57	125	0.703 g/mL	liquid
decane	$C_{10}H_{22}$	–30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.



Figure 12.7.1: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, NASA.gov, Topics, Earth Features, Oil Spill(opens in new window) [www.nasa.gov].

Looking Closer: Gas Densities and Fire Hazards

Table 12.7.1 indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table 12.7.1 are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Looking Closer: An Alkane Basis for Properties of Other Compounds

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called phospholipids and sphingolipids that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.

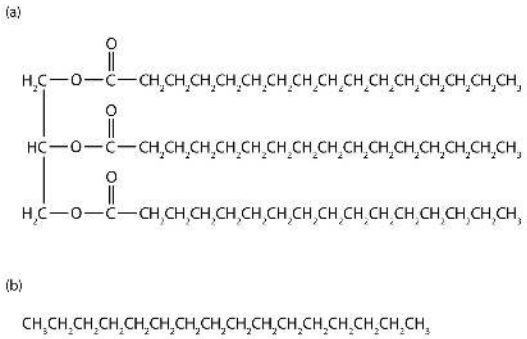


Figure 12.7.2: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

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12.8: Reactions of Alkanes

Learning Objectives

- Understand the reactions of alkanes: combustion and halogenation.

Alkanes are relatively stable, nonpolar molecules, that will not react with acids, bases, or oxidizing or reducing reagents. Alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning "little affinity."

However, heat or light can initiate the breaking of C–H or C–C single bonds in reactions called **combustion** and **halogenation**.

Combustion

Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the **combustion** reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{12.8.1}$$

As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of straight- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure 12.8.1). You may recall that boiling point is a function of intermolecular interactions, which was discussed in an earlier chapter.

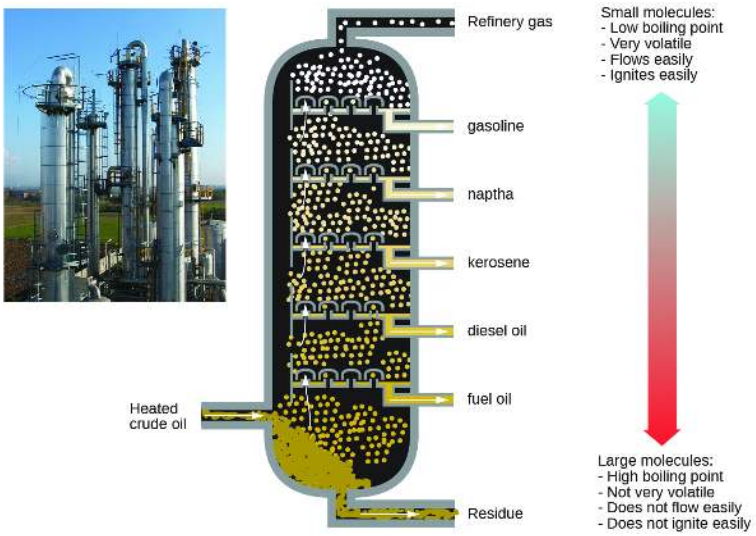


Figure 12.8.1:In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

If the reactants of combustion reactions are adequately mixed, and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and energy—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, other unwanted by-products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{12.8.2}$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Halogenation

In **halogenation** reactions, alkanes react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{12.8.3}$$

With more chlorine, a mixture of products is obtained: CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table 12.8.1, along with some of their uses.

Table 12.8.1: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

Note To Your Health: Halogenated Hydrocarbons

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

Note To Your Health: Chlorofluorocarbons and The Ozone Layer

Alkanes substituted with both fluorine (F) and chlorine (Cl) atoms have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. Two of the best known of these chlorofluorocarbons (CFCs) are listed in Table 12.8.2

Chlorofluorocarbons contribute to the greenhouse effect in the lower atmosphere. They also diffuse into the stratosphere, where they are broken down by ultraviolet (UV) radiation to release Cl atoms. These in turn break down the ozone (O_3) molecules that protect Earth from harmful UV radiation. Worldwide action has reduced the use of CFCs and related compounds. The CFCs and other Cl- or bromine (Br)-containing ozone-destroying compounds are being replaced with more benign substances. Hydrofluorocarbons (HFCs), such as CH_2FCF_3, which have no Cl or Br to form radicals, are one alternative. Another is hydrochlorofluorocarbons (HCFCs), such as $CHCl_2CF_3$. HCFC molecules break down more readily in the troposphere, and fewer ozone-destroying molecules reach the stratosphere.

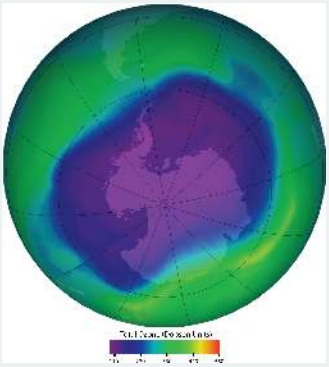


Figure 12.8.2 Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly over Antarctica from late August through early October and fill in about mid-November. Ozone depletion has also been noted over the Arctic regions. The largest ozone hole ever observed occurred on 24 September 2006. Source: Image courtesy of NASA, http://ozonewatch.gsfc.nasa.gov/daily.php?date=2006-09-24.

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12.9: Cycloalkanes

Learning Objectives

- Identify the structures of cycloalkanes.

A **cyclic hydrocarbon** is a hydrocarbon in which the carbon chain joins to itself in a ring. A **cycloalkane** is a cyclic hydrocarbon in which all of the carbon-carbon bonds are single bonds and each carbon is bonded to two hydrogen atoms, they are saturated compounds. Cycloalkanes have the general formula $C_nH_{2\,n}$. The simplest of these cyclic hydrocarbons, cyclopropane, has the formula C_3H_6, which makes a three-carbon ring.

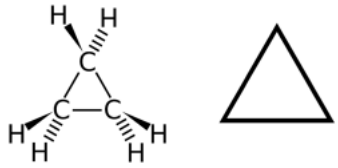
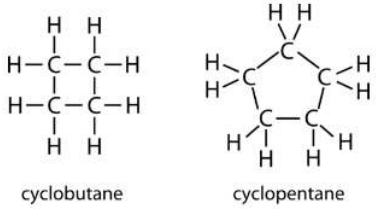


Figure 12.9.1: Cyclopropane is the simplest cycloalkane. Its highly strained geometry makes it rather unstable and highly reactive.

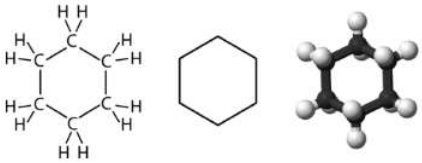
The structural formulas of cyclic hydrocarbons can be represented in multiple ways, two of which are shown above. Each atom can be shown as in the structure on the left from the figure above. A convenient shorthand is to omit the element symbols and only show the shape, as in the triangle on the right. Carbon atoms are understood to be the vertices of the triangle.

The carbon atoms in cycloalkanes have a bond angle of 109.5^{o}. However, an examination of the cyclopropane structure shows that the triangular structure results in a $C-C-C$ bond angle of 60°. This deviation from the ideal angle is called ring strain and makes cyclopropane a fairly unstable and reactive molecule. Ring strain is decreased for cyclobutane, with a bond angle of 90°, but is still significant. Cyclopentane has a bond angle of about 108°. This minimal ring strain for cyclopentane makes it a more stable compound.



cyclobutane cyclopentane

Cyclohexane is a six-carbon cycloalkane, shown below.



All three of the depictions of cyclohexane above are somewhat misleading, because the molecule is not planar. In order to reduce the ring strain and attain a bond angle of approximately 109.5^{o}, the molecule is actually puckered.

The ring structure in cycloalkanes also prevents rotation around the carbon–carbon bonds without breaking open the ring, thus they are more rigid and less flexible than acyclic alkanes. This property is called **restricted rotation**.

Note To Your Health: Cyclopropane as an Anesthetic

With its boiling point of −33°C, cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

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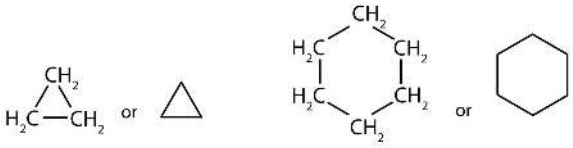
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12.10: Drawing and Naming Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



Some cyclic compounds have substituent groups attached. Example 12.10.1 interprets the name of a cycloalkane with a single substituent group.

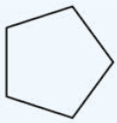
Example 12.10.1

Draw the structure for each compound.

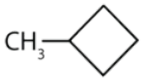
a. cyclopentane
b. methylcyclobutane

Solution

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



- The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.



Exercise 12.10.1

Draw the structure for each compound.

a. cycloheptane
b. ethylcyclohexane

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CHAPTER OVERVIEW

11: Nuclear Chemistry

Most chemists pay little attention to the nucleus of an atom except to consider the number of protons it contains because that determines an element's identity. However, in nuclear chemistry, the composition of the nucleus and the changes that occur there are very important. Applications of nuclear chemistry may be more widespread than you realize. Many people are aware of nuclear power plants and nuclear bombs, but nuclear chemistry also has applications ranging from smoke detectors to medicine, from the sterilization of food to the analysis of ancient artifacts. In this chapter, we will examine some of the basic concepts of nuclear chemistry and some of the nuclear reactions that are important in our everyday lives.

11.6: Ionizing Radiation
11.7: Measuring Radiation
11.8: Artificial Transmutation
11.9: Nuclear Fission and Nuclear Fusion
11.1: Nuclear Reactions
11.2: The Discovery and Nature of Radioactivity
11.3: Stable and Unstable Isotopes
11.4: Nuclear Decay
11.5: Radioactive Half-Life

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11.6: Ionizing Radiation

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle can act as a powerful oxidant.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{11.6.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 11.6.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1\ \text{MeV/particle} = 96\ \text{billion J/mol}. \tag{11.6.2}$$



Figure 11.6.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue.

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 11.6.1.

Table 11.6.1: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
X rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m

*Distance at which half of the radiation has been absorbed.

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure. Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered X rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1 \text{ rad} = 0.010 \text{ J/kg} \qquad 1 \text{ Gy} = 1 \text{ J/kg} \tag{11.6.3}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays.

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing

radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation.

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11.7: Measuring Radiation

Learning Objectives

- Define units for measuring radiation exposure

Radioactivity is determined by measuring the number of decay processes per unit time. Perhaps the easiest way is simply to determine the number of counts/minute, with each count measuring a single decay process, such as the emission of an α-particle. A particular isotope may have an activity of 5,000 counts/minute (cpm) while another isotope might only have $250\ \text{cpm}$. The amount of activity gives a rough indication of the amount of the radioisotope present - the higher the activity, the more radioactivity isotope in the sample.

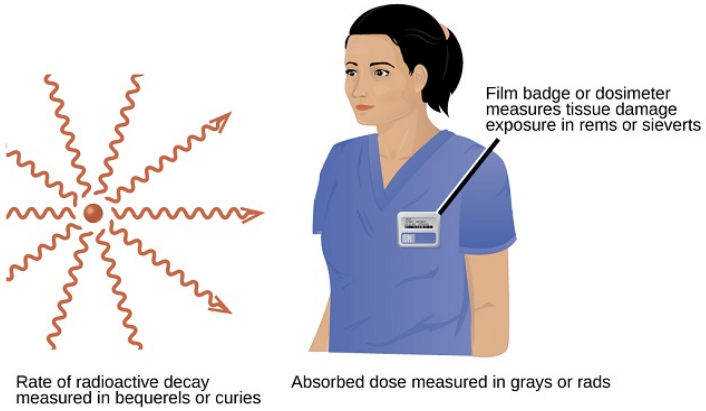


Figure 11.7.1: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC BY 4.0; OpenStax)

Measurement of exposure to radioactivity is important for anyone who deals with radioactive materials on a regular basis. Perhaps the simplest device is a personal **dosimeter** - a film badge that will fog up when exposed to radiation (Figure 11.7.1). The amount of fogging is proportional to the amount of radiation present. These devices are not very sensitive to low levels of radiation. More sensitive systems use crystals that respond in some way to radioactivity by registering the number of emissions in a given time. These systems tend to be more sensitive and more reliable than film badges.

When alpha, beta or gamma particles collides with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this to detect these particles (Figure 11.7.2). In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry.

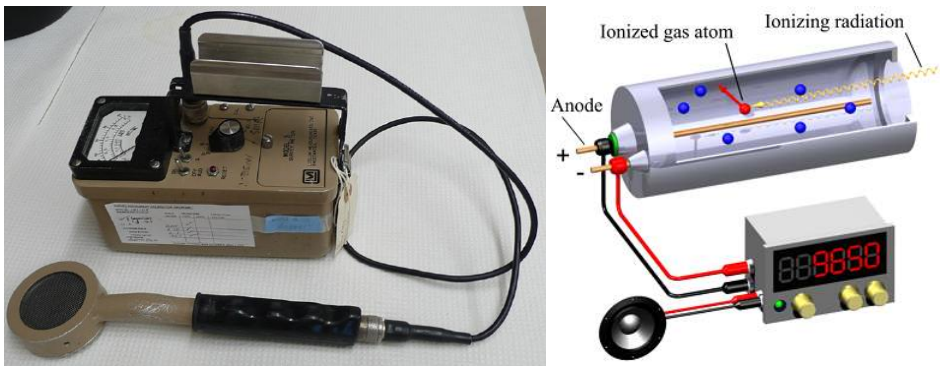


Figure 11.7.2: (left) Geiger counter with pancake type probe. Public Domain; TimVickers via Wikipedia). (right) Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia).

Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter.

We previously used mass to indicate the amount of radioactive substance present. However, this is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation. A variety of units are used to measure various aspects of radiation (Table 11.7.1).

Table 11.7.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for humans (rem)		Rem = RBE × rad

The roentgen equivalent for humans (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:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{11.7.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

The Becquerel Unit

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one **becquerel (Bq).** Even in a small mass of radioactive material, however, there are thousands upon thousands of decays or disintegrations per second. The becquerel is named after Henri Becquerel, who discovered radioactivity in 1896.

The Curie Unit

The **curie** (Ci) is one measure of the rate of decay (named after Pierre and Marie Curie). One curie is equivalent to 3.7×10^{10} disintegrations per second. Since this is obviously a large and unwieldy number, radiation is often expressed in millicuries or microcuries (still very large numbers). The curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena in the early 1900s. The curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 μCi.

The Roentgen Unit

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air.

The Rad Unit

The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1\ rad = 0.010\ J/kg \quad 1\ Gy = 1\ J/kg \tag{11.7.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

The Gray Unit

Another unit of radiation absorption is the **gray (Gy)**:

$$1 \text{ Gy} = 100 \text{ rad}$$

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of H_2O (approximately the same mass as a 150 lb person) would increase its temperature by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1×10^{21} molecular C–C bonds in a person's body. That amount of damage would not be desirable.

The Rem Unit

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in human)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor:

$$em = rad \times RBE \tag{11.7.3}$$

where RBE is the *relative biological effectiveness factor* is a number greater than or equal to 1 that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, RBE factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye tissue, the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X ray is about 20 mrem.

The Sievert Unit

A sievert (Sv) is related to the rem unit and is defined as 100 rem. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 11.7.2. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 11.7.2: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women

Dose (rem)	Symptoms/Effects
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Which of the two is applicable to humans?

According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

Summary

The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

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11.8: Artificial Transmutation

Learning Objectives

- Describe transmutation.
- Write and balance transmutation equations.

Although the conversion of one element to another is the basis of natural radioactive decay, it is also possible to convert one element to another artificially. The conversion of one element to another is the process of **transmutation**. Between 1921 and 1924, Patrick Blackett conducted experiments in which he converted a stable isotope of nitrogen to a stable isotope of oxygen. By bombarding ^{14}N with α particles he created ^{17}O. Transmutation may also be accomplished by bombardment with neutrons.

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \rightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$

The $^{17}_{8}\text{O}$ and $^{1}_{1}\text{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure 11.8.1). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.



Figure 11.8.1: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2103 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$\begin{aligned} {}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} &\longrightarrow {}^{239}_{92}\text{U} \\ {}^{239}_{92}\text{U} &\longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e} \qquad \text{half-life} = 23.5 \text{ min} \\ {}^{239}_{93}\text{Np} &\longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e} \qquad \text{half-life} = 2.36 \text{ days} \end{aligned}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$$ {}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \xrightarrow{\beta^-} {}^{239}_{93}\text{Np} \xrightarrow{\beta^-} {}^{239}_{94}\text{Pu} \tag{11.8.1}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 11.8.1.

Table 11.8.1: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	${}^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^{0}_{-1}\text{e}$
curium	Cm	96	${}^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
californium	Cf	98	${}^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{243}_{97}\text{Bk} + 2\,{}^{1}_{0}\text{n}$
einsteinium	Es	99	${}^{238}_{92}\text{U} + 15\,{}^{1}_{0}\text{n} \longrightarrow {}^{253}_{99}\text{Es} + 7\,{}^{0}_{-1}\text{e}$
mendelevium	Md	101	${}^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
nobelium	No	102	${}^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4\,{}^{1}_{0}\text{n}$
rutherfordium	Rf	104	${}^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4\,{}^{1}_{0}\text{n}$
seaborgium	Sg	106	${}^{206}_{82}\text{Pb} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{257}_{106}\text{Sg} + 3\,{}^{1}_{0}\text{n}$ ${}^{249}_{98}\text{Cf} + {}^{18}_{8}\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4\,{}^{1}_{0}\text{n}$
meitnerium	Mt	107	${}^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^{1}_{0}\text{n}$

Example 11.8.1

Write the balanced nuclear equation for the production of the following transuranium elements:

a. berkelium-244, made by the reaction of Am-241 and He-4
b. fermium-254, made by the reaction of Pu-239 with a large number of neutrons
c. lawrencium-257, made by the reaction of Cf-250 and B-11
d. dubnium-260, made by the reaction of Cf-249 and N-15

Solution

a

From the given information we can write the nuclear equation

$${}^{241}_{95}\text{Am} + {}^{4}_{2}\text{He} \rightarrow {}^{244}_{97}\text{Bk}$$

On the left side the total mass number is

$$241 + 4 = 245$$

and the total atomic number is

$$95 + 2 = 97$$

On the right side the total mass number is 244 and the total atomic number is 97. This shows that one neutron needs to be added which would increase the total mass number needs to by one while keeping the total atomic number the same. The balanced nuclear equation would be

$$^{241}_{95}\mathrm{Am} + ^{4}_{2}\mathrm{He} \rightarrow ^{244}_{97}\mathrm{Bk} + ^{1}_{0}\mathrm{n}$$

b

From the given information we can write the nuclear equation

$$^{239}_{94}\mathrm{Pu} + \mathrm{x}\ ^{1}_{0}\mathrm{n} \rightarrow ^{254}_{100}\mathrm{Fm}$$

On the left side we see that the total mass number is the sum of $239 + (1)\mathrm{x}$. on the right side we see that the total mass number is 254. since the total mass number of the reactants must equal that of the products we can write

$$239 + \mathrm{x} = 254$$

showing 15 neutrons need to be added to balance the mass number.

$$^{239}_{94}\mathrm{Pu} + 15\ ^{1}_{0}\mathrm{n} \rightarrow ^{254}_{100}\mathrm{Fm}$$

To balance the total atomic number of the equation, 6 electrons need to be added to the right side. Therefore the balanced equation reads:

$$^{239}_{94}\mathrm{Pu} + 15\ ^{1}_{0}\mathrm{n} \rightarrow ^{254}_{100}\mathrm{Fm} + 6\ ^{0}_{-1}\mathrm{e}$$

c

From the given information we can write the nuclear equation

$$^{250}_{98}\mathrm{Cf} + ^{11}_{5}\mathrm{B} \rightarrow ^{257}_{103}\mathrm{Lr}$$

On the left side the total mass number is

$$250 + 11 = 261$$

and the total atomic number is

$$98 + 5 = 103$$

On the right side the total mass number is 257 and the total atomic number is 103. This means that 4 neutrons need to be added to the right side to balance the equation. The balanced nuclear equation is

$$^{250}_{98}\mathrm{Cf} + ^{11}_{5}\mathrm{B} \rightarrow ^{257}_{103}\mathrm{Lr} + 4\ ^{1}_{0}\mathrm{n}$$

d

From the given information we can write the nuclear equation

$$^{249}_{98}\mathrm{Cf} + ^{15}_{7}\mathrm{N} \rightarrow ^{260}_{105}\mathrm{Db}$$

On the left side the total mass number is

$$249 + 15 = 264$$

and the total atomic number is

$$98 + 7 = 105$$

On the right side the total mass number is 260 and the total atomic number is 105. This means that 4 neutrons need to be added to the right side t obalance the equation. The balanced nuclear equation is

$$^{249}_{98}\mathrm{Cf} + {}^{15}_{7}\mathrm{N} \rightarrow {}^{260}_{105}\mathrm{Lr} + 4\ {}^{1}_{0}\mathrm{n}$$

Contributors and Attributions

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11.9: Nuclear Fission and Nuclear Fusion

Learning Objectives

- Explain nuclear fission and fusion processes.
- Write and balance nuclear fission and fusion equations.
- Relate the concepts of critical mass and nuclear chain reactions.

Nuclear fusion and **nuclear fission** are two different types of energy-releasing reactions in which energy is released from high-powered atomic bonds between the particles within the nucleus. The main difference between these two processes is that fission is the splitting of an atom into two or more smaller ones while fusion is the fusing of two or more smaller atoms into a larger one.

Protons and neutrons make up a nucleus, which is the foundation of nuclear science. Fission and fusion involves the dispersal and combination of elemental nucleus and isotopes, and part of nuclear science is to understand the process behind this phenomenon. Adding up the individual masses of each of these subatomic particles of any given element will always give you a greater mass than the mass of the nucleus as a whole. The missing idea in this observation is the concept called nuclear binding energy. Nuclear binding energy is the energy required to keep the protons and neutrons of a nucleus intact, and the energy that is released during a nuclear fission or fusion is nuclear power. There are some things to consider however. The mass of an element's nucleus as a whole is less than the total mass of its individual protons and neutrons.

To calculate the energy released during mass destruction in both nuclear fission and fusion, we use Einstein's equation that equates energy and mass:

$$E = mc^2 \tag{11.9.1}$$

with m is mass (kilograms), c is speed of light (meters/sec) and E is energy (Joules).

Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 11.9.1.

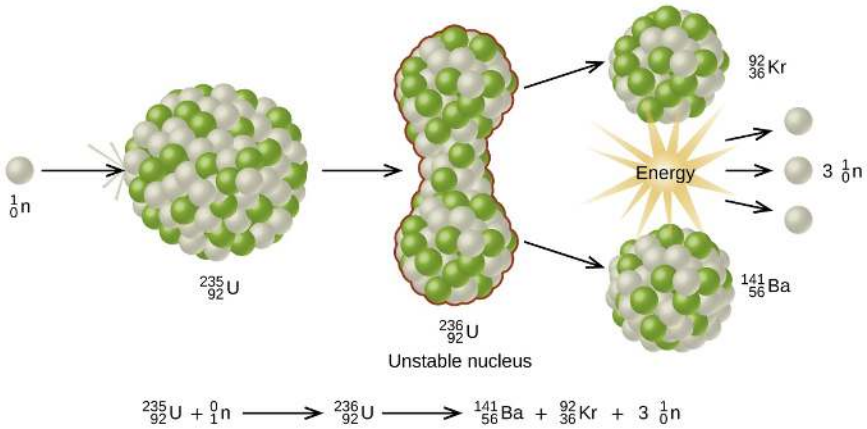


Figure 11.9.1: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 11.9.2 Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

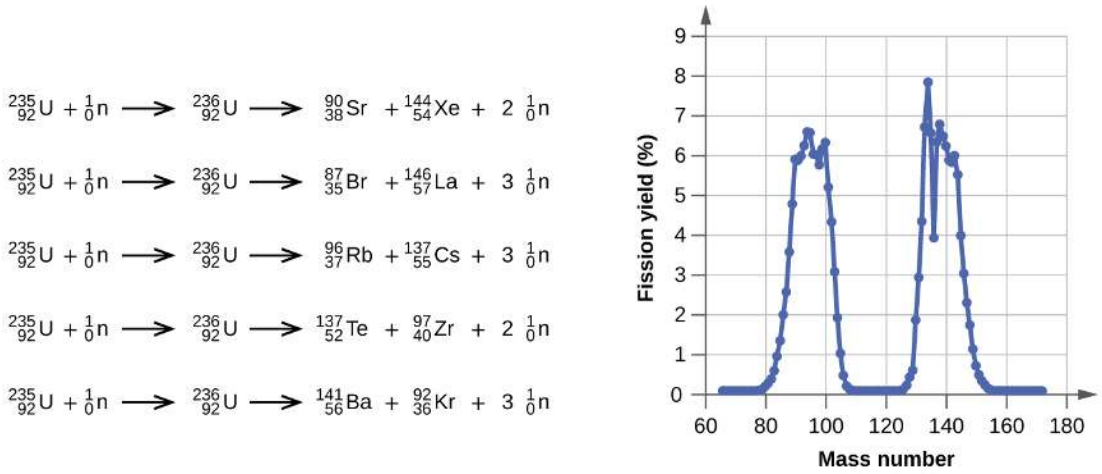


Figure 11.9.2: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

When undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure 11.9.3). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

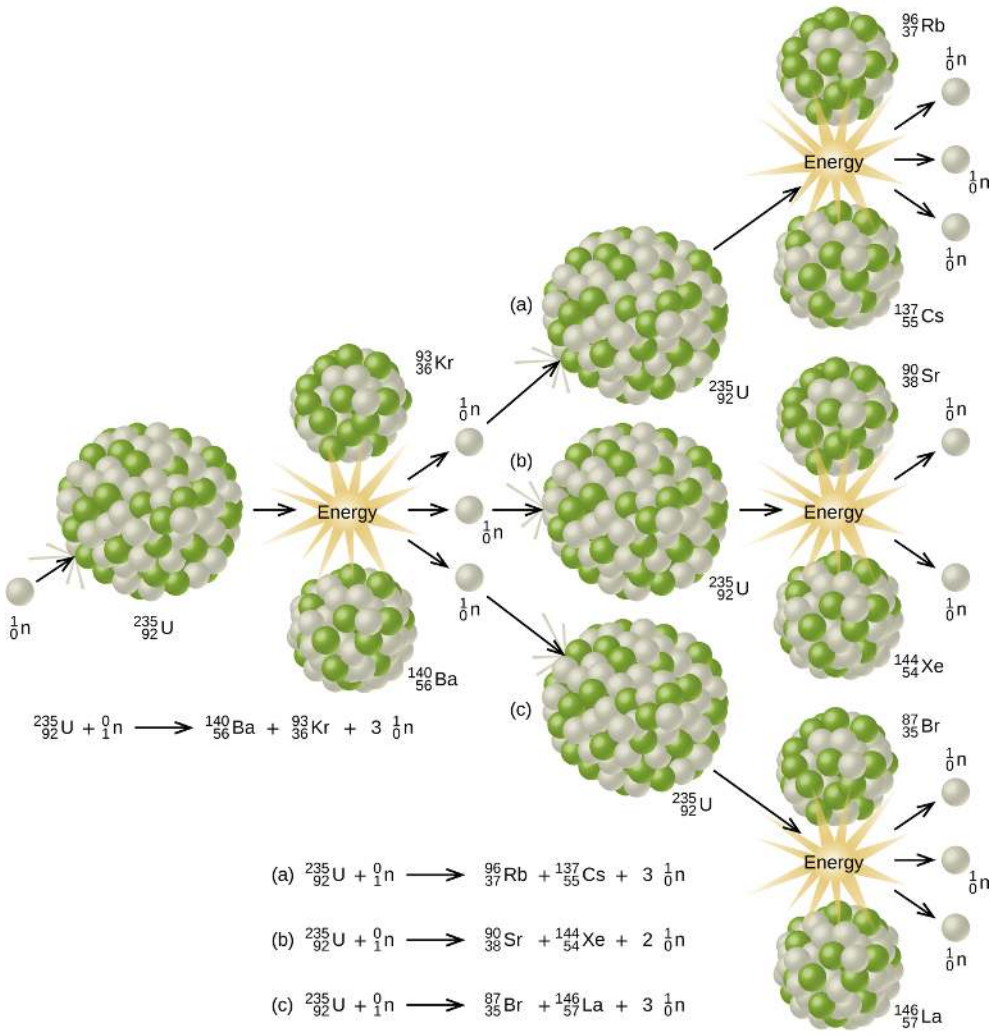


Figure 11.9.3: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a **critical mass**. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down.

The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g)$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 11.9.4).

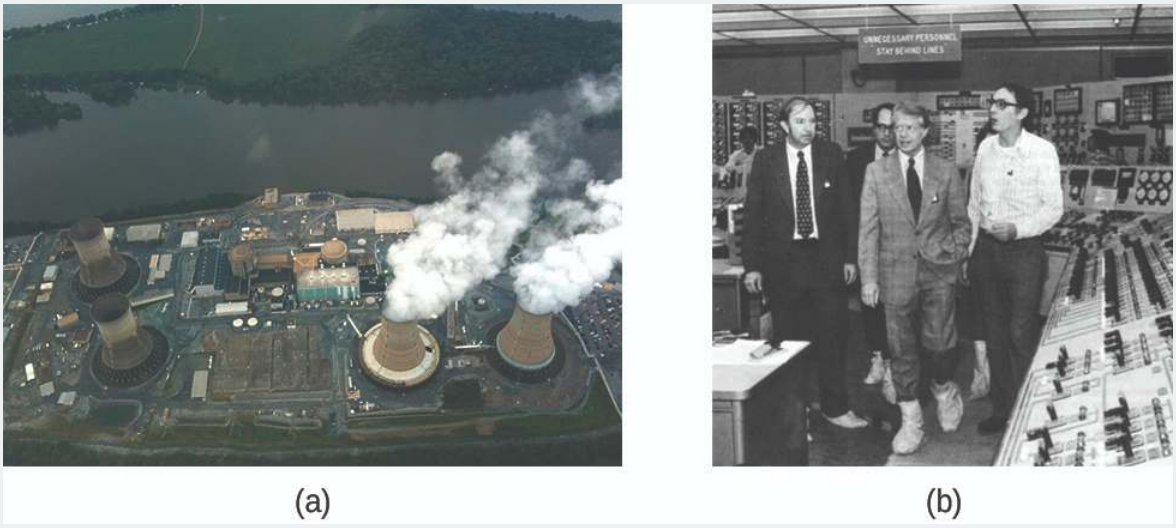


Figure 11.9.4: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan’s nuclear power plants were subsequently shut down, remaining shuttered as of

December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 11.9.5).



Figure 11.9.5: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Nuclear Fusion

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1} \tag{11.9.2}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^{4}_{2}\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^{2}_{1}$ and a triton, ${}^{3}_{1}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n} \tag{11.9.3}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^{9} kilojoules per mole of ${}^{4}_{2}\mathrm{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

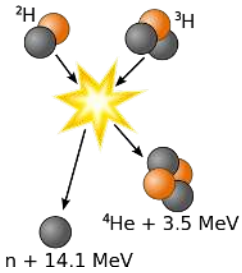


Figure 11.9.6: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure 11.9.7).

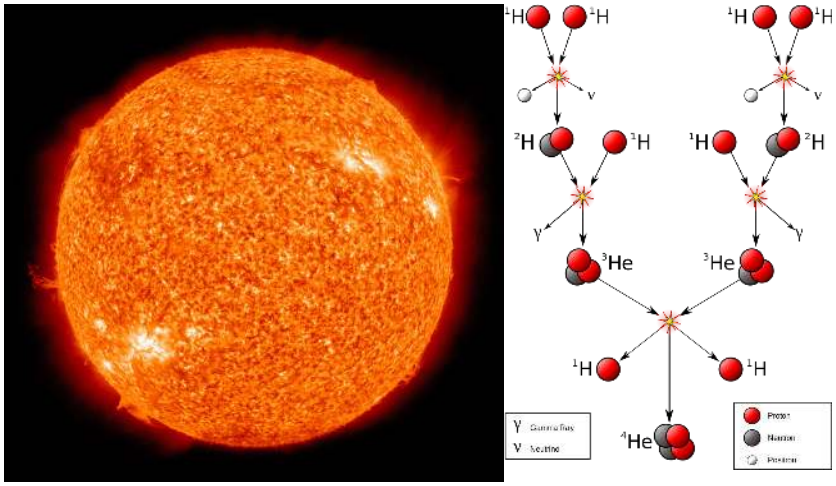


Figure 11.9.7: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 11.9.1

Calculate the energy released in each of the following hypothetical processes.

a. $3\,{}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C}$
b. $6\,{}^{1}_{1}\mathrm{H} + 6\,{}^{1}_{0}\mathrm{n} \rightarrow {}^{12}_{6}\mathrm{C}$
c. $6\,{}^{2}_{1}\mathrm{D} \rightarrow {}^{12}_{6}\mathrm{C}$

Solution

a. $Q_a = 3 \times 4.0026 - 12.000)\,amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.17 \times 10^{-12}\ J$
b. $Q_b = (6 \times (1.007825 + 1.008665) - 12.00000)\,amu \times (1.4924 \times 10^{1-0} J/amu) = 1.476 \times 10^{-11}\ J$
c. $Q_c = 6 \times 2.014102 - 12.00000\,amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.263 \times 10^{-11}\ J$

Fusion of He to give C releases the least amount of energy, because the fusion to produce He has released a large amount. The difference between the second and the third is the binding energy of deuterium. The conservation of mass-and-energy is well illustrated in these calculations. On the other hand, the calculation is based on the conservation of mass-and-energy.

Nuclear Reactors

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

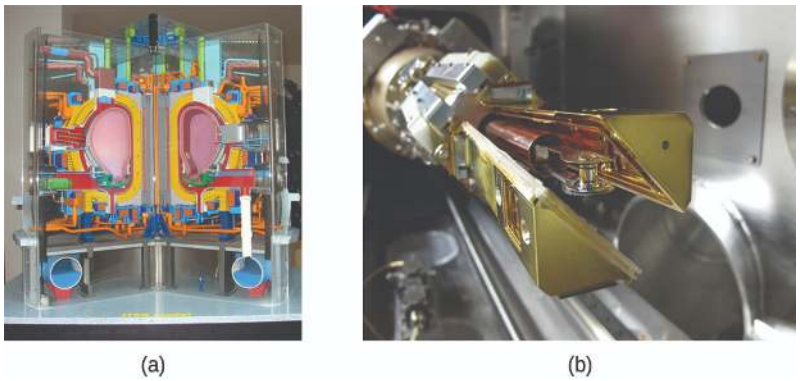


Figure 11.9.8: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving larg\times 10^{scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 11.9.8). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

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11.1: Nuclear Reactions

Learning Objectives

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Identify a nuclear reaction
- Identify the key characteristics separating nuclear and chemical reactions

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of ${}^{1}_{1}\text{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation:

$$ {}^{\text{A}}_{\text{Z}}\text{X} \tag{11.1.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, ${}^{14}_{6}\text{C}$ is called "carbon-14." The element in this example, represented by the symbol *C*, is carbon. Its atomic number, 6, is the lower left subscript on the symbol and is the number of protons in the atom. The mass number, the superscript to the upper left of the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 14, which means that the number of neutrons in the atom is 14 − 6 = 8 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neutrons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. The two isotopes of hydrogen, ${}^{2}\text{H}$ and ${}^{3}\text{H}$, are given their own names: deuterium (D) and tritium (T), respectively. Another way of expressing a particular isotope is to list the mass number after the element name, like carbon-12 or hydrogen-3.

Nuclear reactions are very different from chemical reactions. In chemical reactions, atoms become more stable by participating in a transfer of electrons or by sharing electrons with other atoms. In **nuclear reactions**, it is the nucleus of the atom that gains stability by undergoing a change of some kind. The energies that are released in nuclear reactions are many orders of magnitude greater than the energies involved in chemical reactions. Unlike chemical reactions, nuclear reactions are not noticeably affected by changes in environmental conditions, such as temperature or pressure.

As the following Sections will discuss, there are three main forms of radioactive emissions. The first is called an alpha particle,which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use ${}^{4}_{2}\text{He}$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a **nuclear equation**—for example, the alpha-particle emission of uranium-235 is as follows:

$$ {}^{235}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{231}_{90}\text{Th} \tag{11.1.2}$$

Chemists often use the names **parent isotope** and **daughter isotope** to represent the original atom and the product other than the alpha particle. In the previous example, ${}^{235}_{92}\text{U}$ is the parent isotope, and ${}^{231}_{90}\text{Th}$ is the daughter isotope. When one element changes into another in this manner, it undergoes *radioactive decay*.

Major Differences between Nuclear and Chemical Reactions

1. Nuclear reactions involve a change in an atom's nucleus, usually producing a different element. Chemical reactions, on the other hand, involve only a rearrangement of electrons and do not involve changes in the nuclei.

2. Different isotopes of an element normally behave similarly in chemical reactions. The nuclear chemistry of different isotopes vary greatly from each other.
3. Rates of chemical reactions are influenced by temperature and catalysts. Rates of nuclear reactions are unaffected by such factors.
4. Nuclear reactions are independent of the chemical form of the element.
5. Energy changes accompanying nuclear reactions are much larger. This energy comes from destruction of mass.
6. In a nuclear reaction, mass is not strictly conserved. Some of the mass is converted into energy.

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11.2: The Discovery and Nature of Radioactivity

Learning Objectives

- To define and give examples of the major types of radioactivity.

Atomic theory in the 19th century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source as the atomic nucleus. These emanations were ultimately called, collectively, **radioactivity**.

There are three main forms of radioactive emissions. The first is called an **alpha particle**,which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use ${}^{4}_{2}\text{He}$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a nuclear equation—for example, the alpha-particle emission of uranium-235 is as follows:

$$ {}^{235}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{231}_{90}\text{Th} \tag{11.2.1}$$

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure 11.2.1) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β **particles**; and a third was uncharged electromagnetic waves, γ **rays**. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

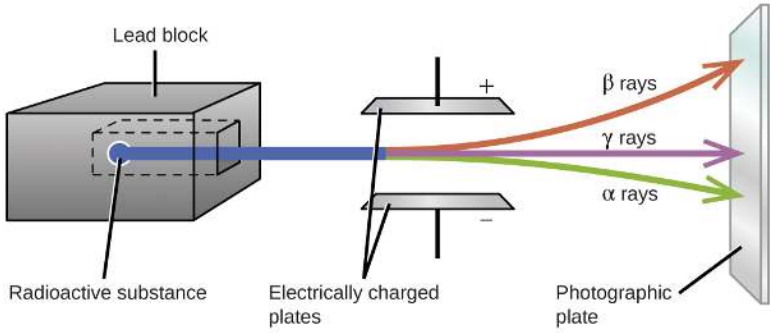


Figure 11.2.1: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged. (CC BY 4.0; OpenStax)

Alpha, beta, and gamma emissions have different abilities to penetrate matter (Figure 11.2.2). The relatively large alpha particle is easily stopped by matter (although it may impart a significant amount of energy to the matter it contacts). Beta particles penetrate slightly into matter, perhaps a few centimeters at most. Gamma rays can penetrate deeply into matter and can impart a large amount of energy into the surrounding matter. Table 11.2.1 summarizes the properties of the three main types of radioactive emissions.

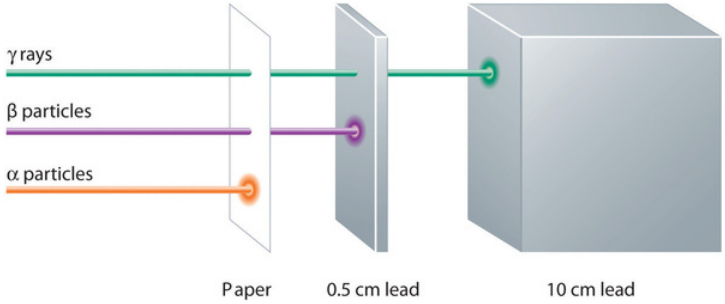


Figure 11.2.2: Different emissions exhibit different pentration powers. (CC BY-NC-SA 3.0; anonymous)

Table 11.2.1: The Three Main Forms of Radioactive Emissions

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	α, $^{4}_{2}\mathrm{He}$	β, $^{0}_{-1}\mathrm{e}$	γ
identity	helium nucleus	electron	electromagnetic radiation
charge	2+	1−	none
mass number	4	0	0
penetrating power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

Key Takeaway

The major types of radioactivity include alpha particles, beta particles, and gamma rays.

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11.3: Stable and Unstable Isotopes

Learning Outcomes

- Recognize that radioactivity is a signature of unstable nuclide - radioisotopes.
- Describe a radioisotope.
- Explain how the stability of isotopes depends on the composition of its nucleus.
- Use the "band of stability" to identify stable isotopes.

The discovery of radioactivity and its effects on the nuclei of elements disproved Dalton's assumption that atoms are indivisible. A **nuclide** *is a term for an atom with a specific number of protons and neutrons in its nucleus.* When nuclides of one type emit radiation, they are changed into different nuclides. Radioactive decay is spontaneous and does not required an input of energy to occur. The stability of a particular nuclide depends on the composition of its nucleus, including the number of protons, the number of neutrons, and the proton-to-neutron ratio.

In nuclear reactions, it is the nucleus of the atom that gains stability by undergoing a change of some kind. Some elements have no stable isotopes, which means that any atom of that element is radioactive. For some other elements, only certain isotopes are radioactive. A **radioisotope** *is an isotope of an element that is unstable and undergoes radioactive decay*. The energies that are released in nuclear reactions are many orders of magnitude greater than the energies involved in chemical reactions. Unlike chemical reactions, nuclear reactions are not noticeably affected by changes in environmental conditions, such as temperature or pressure.

Carbon-12, with six protons and six neutrons, is a *stable* nucleus, meaning that it does not spontaneously emit radioactivity. Carbon-14, with six protons and eight neutrons, is *unstable* and naturally radioactive. Among atoms with lower atomic numbers, the ideal ratio of neutrons to protons is approximately 1:1. As the atomic number increases, the stable neutron-proton ratio gradually increases to about 1.5:1 for the heaviest known elements. For example, lead-206 is a stable nucleus that contains 124 neutrons and 82 protons, a ratio of 1.51 to 1.

This observation is shown in Figure 11.3.1. The **band of stability** *is the range of stable nuclei on a graph that plots the number of neutrons in a nuclide against the number of protons.* Known stable nuclides are shown with individual blue dots, while the 1:1 and 1.5:1 ratios are shown with a solid red line and a green line, respectively.

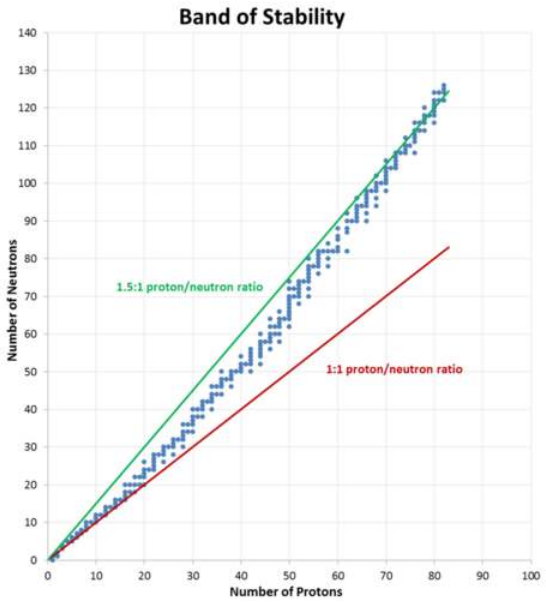


Figure 11.3.1: A graph of the number of neutrons in a nucleus as a function of the number of protons. Each known stable nucleus is represented by a blue dot. The ideal neutron to proton ratio changes from 1:1 for light nuclei to 1.5:1 for the heaviest nuclei.

It should be noted that just because a nucleus is "unstable" (able to undergo spontaneous radioactive decay) does not mean that it will rapidly decompose. For example, uranium-238 is unstable because it spontaneously decays over time, but if a sample of

uranium-238 is allowed to sit for 1000 years, only $0.0000155\%$of the sample will have decayed. However, other unstable nuclei, such as berkelium-243, will be almost completely gone ($>99.9999\%$decayed) in less than a day.

Contributors and Attributions

-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

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11.4: Nuclear Decay

Learning Objectives

- Write and balance nuclear equations.

Unstable nuclei spontaneously emit radiation in the form of particles and energy. This generally changes the number of protons and/or neutrons in the nucleus, resulting in a more stable nuclide. One type of a nuclear reaction is **radioactive decay**, *a reaction in which a nucleus spontaneously disintegrates into a slightly lighter nucleus, accompanied by the emission of particles, energy, or both.* An example is shown below, in which the nucleus of a polonium atom radioactively decays into a lead nucleus.

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{11.4.1}$$

Note that in a balanced nuclear equation, the sum of the atomic numbers (subscripts) and the sum of the mass numbers (superscripts) must be equal on both sides of the equation. How do we know that a product of the reaction is $^{231}_{90}\mathrm{Th}$? We use a modified type of the **law of conservation of matter**, which says that we must have the same number of protons and neutrons on both sides of the chemical equation. If our uranium nucleus loses 2 protons from the alpha particle, then there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose 4 nuclear particles of the original 235, there are 231 remaining. Thus, we use subtraction to identify the isotope of the thorium atom—in this case, $^{231}_{90}\mathrm{Th}$.

Because the number of protons changes as a result of this nuclear reaction, the identity of the element changes. **Transmutation** *is a change in the identity of a nucleus as a result of a change in the number of protons.* There are several different types of naturally occurring radioactive decay, and we will examine each separately.

Alpha Emission

An **alpha particle** (α) *is a helium nucleus with two protons and two neutrons.* Alpha particles are emitted during some types of radioactive decay. The net charge of an alpha particle is $2+$, and its mass is approximately $4\ \mathrm{amu}$. The symbol for an alpha particle in a nuclear equation is usually $^{4}_{2}\mathrm{He}$, though sometimes α is used. Alpha emission typically occurs for very heavy nuclei in which the nuclei are unstable due to large numbers of nucleons. For nuclei that undergo alpha decay, their stability is increased by the subtraction of two protons and two neutrons. For example, uranium-238 decays into thorium-234 by the emission of an alpha particle (see Figure 11.4.1).

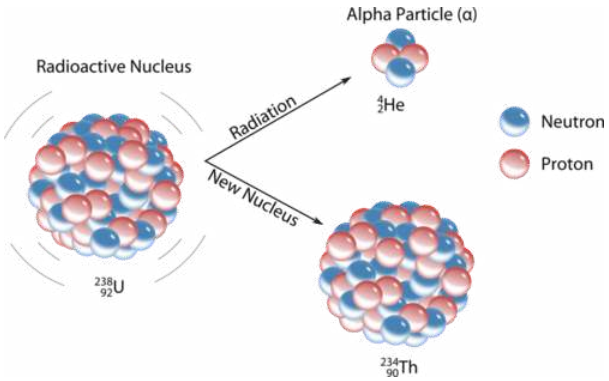


Figure 11.4.1: The unstable uranium-238 nucleus spontaneously decays into a thorium-234 nucleus by emitting an alpha particle.

Example 11.4.1: Radon-222

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as $^{222}_{86}\mathrm{Rn}$. We represent the alpha particle as $^{4}_{2}\mathrm{He}$ and use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as an isotope of polonium, $^{218}_{84}\mathrm{Po}$:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{218}_{84}\mathrm{Po}$$

Exercise 11.4.1: Polonium-209

Write the nuclear equation that represents the radioactive decay of polonium-209 by alpha particle emission and identify the daughter isotope.

Answer

$$^{209}_{84}\text{Po} \rightarrow {}^{4}_{2}\text{He} + {}^{205}_{82}\text{Pb}$$

Beta Emission

Nuclei above the band of stability are unstable because their neutron to proton ratio is too high. To decrease that ratio, a neutron in the nucleus is capable of turning into a proton and an electron. The electron is immediately ejected at a high speed from the nucleus. A **beta particle** (β) *is a high-speed electron emitted from the nucleus of an atom during some kinds of radioactive decay* (see Figure 11.4.2). The symbol for a beta particle in an equation is either β or $^{0}_{-1}\text{e}$. Carbon-14 undergoes beta decay, transmutating into a nitrogen-14 nucleus.

$$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e} \tag{11.4.2}$$

Note that beta decay increases the atomic number by one, but the mass number remains the same.

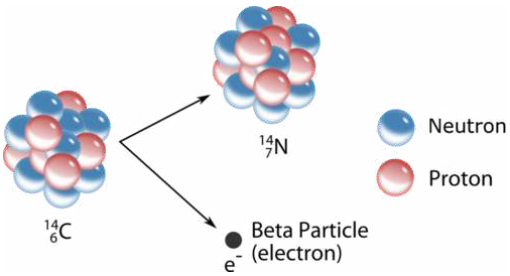


Figure 11.4.2: The beta emission of a carbon-14 nuclide involves the conversion of a neutron to a proton and an electron, with the electron being emitted from the nucleus.

Example 11.4.2: Boron-12

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is $^{12}_{5}\text{B}$ while one of the products is an electron, $^{0}_{-1}\text{e}$. So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus, the complete nuclear equation is as follows:

$$^{12}_{5}\text{B} \rightarrow {}^{12}_{6}\text{C} + {}^{0}_{-1}\text{e} + \gamma$$

The daughter isotope is $^{12}_{6}\text{C}$.

Exercise 11.4.2: Iodine-131

Write the nuclear equation that represents the radioactive decay of iodine-131 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Answer

$$^{131}_{53}\text{I} \rightarrow {}^{131}_{54}\text{Xe} + {}^{0}_{-1}\text{e} + \gamma$$

Gamma Emission

Gamma rays (γ) *are very high energy electromagnetic waves emitted from a nucleus.* Gamma rays are emitted by a nucleus when nuclear particles undergo transitions between nuclear energy levels. This is analogous to the electromagnetic radiation emitted when excited electrons drop from higher to lower energy levels; the only difference is that nuclear transitions release much more energetic radiation. Gamma ray emission often accompanies the decay of a nuclide by other means.

$$^{230}_{90}\text{Th} \rightarrow {}^{226}_{88}\text{Ra} + {}^{4}_{2}\text{He} + \gamma \tag{11.4.3}$$

The emission of gamma radiation has no effect on the atomic number or mass number of the products, but it reduces their energy.

Positron Emission

Nuclei below the band of stability are unstable because their neutron to proton ratio is too low. One way to increase that ratio is for a proton in the nucleus to turn into a neutron and another particle called a positron. A **positron** *is a particle with the same mass as an electron, but with a positive charge*. Like the beta particle, a positron is immediately ejected from the nucleus upon its formation. The symbol for a positron in an equation is $^{0}_{+1}\text{e}$. For example, potassium-38 emits a positron, becoming argon-38.

$$^{38}_{19}\text{K} \rightarrow {}^{38}_{18}\text{Ar} + {}^{0}_{1}\text{e} \tag{11.4.4}$$

Positron emission decreases the atomic number by one, but the mass number remains the same.

Electron Capture

An alternate way for a nuclide to increase its neutron to proton ratio is by a phenomenon called **electron capture**, sympolized E.C. In electron capture, an electron from an inner orbital is captured by the nucleus of the atom and combined with a proton to form a neutron. For example, silver-106 undergoes electron capture to become palladium-106.

$$^{106}_{47}\text{Ag} + {}^{0}_{-1}\text{e} \rightarrow {}^{106}_{46}\text{Pd} \tag{11.4.5}$$

Note that the overall result of electron capture is identical to positron emission. The atomic number decreases by one while the mass number remains the same.

Summary of Nuclear Radiation

Table 11.4.1lists the characteristics of the different types of radioactive decay.

Table 11.4.1 *Summary of types of radioactive decay.*

Type	Symbol	Change in Atomic Number	Change in Mass Number	Change in Number of Neutrons
Alpha emission	$^{4}_{2}\text{He}$ or α	–2	–4	–2
Beta emission	$^{0}_{-1}\text{e}$ or β	+1	0	–1
Gamma emission	γ or $^{0}_{0}\gamma$	0	0	0
Positron emission	$^{0}_{1}\text{e}$ or β^{+}	–1	0	+1
electron capture	E.C.	–1	0	+1

Example 11.4.3

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\text{S}$
b. the decay of $^{201}_{80}\text{Hg}$ by electron capture
c. the decay of $^{30}_{15}\text{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ${}^{A}_{Z}\mathrm{X}$:

$$ {}^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta $$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$ {}^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta $$

b.

A We know the identities of both reactants: ${}^{201}_{80}\mathrm{Hg}$ and an inner electron, ${}^{0}_{-1}\mathrm{e}$. The reaction is as follows:

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z}\mathrm{X} $$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{201}_{79}\mathrm{Au} $$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$ {}^{30}_{15}\mathrm{P} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{+1}\beta $$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$ {}^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta $$

? Exercise 11.4.3

Write a balanced nuclear equation to describe each reaction.

a. ${}^{11}_{6}\mathrm{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from ${}^{185}_{74}\mathrm{W}$

Answer a

$$ {}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta $$

Answer d

$$ {}^{99}_{42}\mathrm{Mo} \rightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\beta $$

Answer c

$$ {}^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma $$

Example 11.4.4

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\text{Ti}$
b. $^{242}_{94}\text{Pu}$
c. $^{12}_{5}\text{B}$
d. $^{256}_{100}\text{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\text{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\text{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\text{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise 11.4.4

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\text{Si}$
b. $^{43}_{21}\text{Sc}$
c. $^{231}_{91}\text{Pa}$

Answer a

beta decay

Answer d

positron emission or electron capture

Answer c

alpha decay

Contributors and Attributions

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11.5: Radioactive Half-Life

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.
- Describe common radiometric carbon-14 dating technique.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life** ($t_{1/2}$), which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

Each radioactive nuclide has a characteristic, constant half-life ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60 source, since half of the $^{60}_{27}\text{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

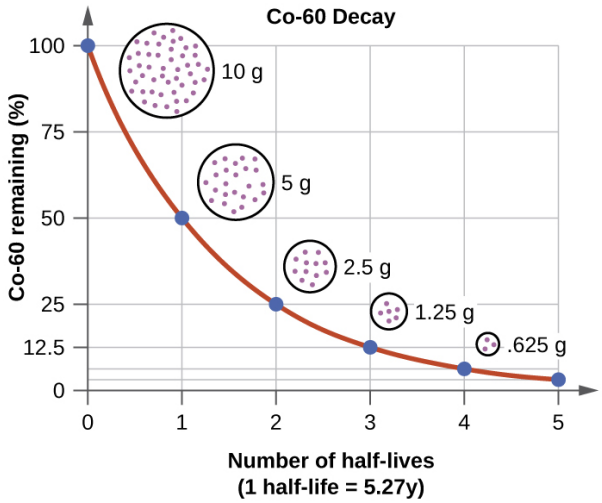


Figure 11.5.1: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on. (CC BY 4.0; OpenStax)

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{n} \tag{11.5.1}$$

where n is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example : Fluorine-20

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so using the previous expression, n = 4. Substituting and solving results in the following:

$$\begin{aligned}\text{amount remaining} &= 5.00\,g \times \left(\frac{1}{2}\right)^4 \\ &= 5.00\,g \times \left(\frac{1}{16}\right) \\ &= 0.313\,g\end{aligned}$$

Less than one-third of a gram of fluorine-20 remains.

Exercise : Titanium-44

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer

0.0375 g

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table 11.5.1- Half-Lives of Various Isotopes, lists the half-lives of some isotopes.

Table 11.5.1 Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5730 y
^{40}K	1.26×10^{9} y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^{8} y
^{238}U	4.47×10^{9} y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Chemistry Is Everywhere: Radioactive Elements in the Body

You may not think of yourself as radioactive, but you are. A small portion of certain elements in the human body are radioactive and constantly undergo decay. Most of the radioactivity in the human body comes from potassium-40 and carbon-14. Potassium and carbon are two elements that we absolutely cannot live without, so unless we can remove all the radioactive isotopes of these elements, there is no way to escape at least some radioactivity. There is debate about which radioactive element is more problematic. There is more potassium-40 in the body than carbon-14, and it has a much longer half-life. Potassium-40 also decays with about 10 times more energy than carbon-14, making each decay potentially more problematic. However, carbon is the element that makes up the backbone of most living molecules, making carbon-14 more likely to be present around important molecules, such as proteins and DNA molecules. Most experts agree that while it is foolhardy to expect absolutely no exposure to radioactivity, we can and should minimize exposure to excess radioactivity.

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or **carbon-14 dating**, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: ${}^{12}_{6}\mathrm{C}$, which constitutes about 99% of the carbon on earth; ${}^{13}_{6}\mathrm{C}$, about 1% of the total; and trace amounts of ${}^{14}_{6}\mathrm{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$ {}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} $$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of ${}^{14}_{6}\mathrm{CO}_2$ to ${}^{12}_{6}\mathrm{CO}_2$ depends on the ratio of ${}^{14}_{6}\mathrm{CO}$ to ${}^{12}_{6}\mathrm{CO}$ in the atmosphere. The natural abundance of ${}^{14}_{6}\mathrm{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of ${}^{14}_{6}\mathrm{C}{}^{14}_{6}\mathrm{CO}_2$ and ${}^{12}_{6}\mathrm{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio found in a living plant is the same as the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because ${}^{12}_{6}\mathrm{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$ {}^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e} $$

Thus, the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure $11.5.2$visually depicts this process.

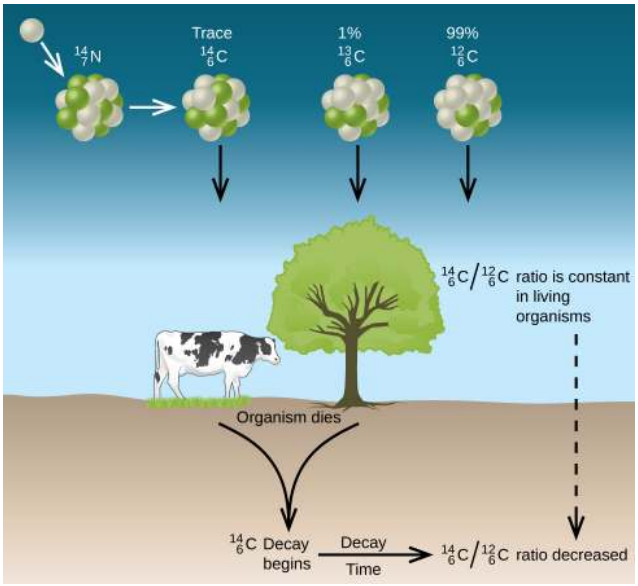


Figure 11.5.2: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). (CC BY 4.0; OpenStax)

For example, with the half-life of ${}^{14}_{6}\mathrm{C}$ being 5730 years, if the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

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