# INTRODUCTORY CHEMISTRY FOR ALLIED HEALTH



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# Chemistry for Allied Health (Chan)

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## Glossary

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# Licensing

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# CHAPTER OVERVIEW

## 1: Chemistry, Matter, and Measurement

The study of chemistry will open your eyes to a fascinating world. Chemical processes are continuously at work all around us. They happen as you cook and eat food, strike a match, shampoo your hair, and even read this page. Chemistry is called the central science because a knowledge of chemical principles is essential for other sciences. You might be surprised at the extent to which chemistry pervades your life.


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Thumbnail: Two small test tubes held in spring clamps. (CC BY-SA 3.0; mitchell125).

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# 1.1: Prelude to Chemistry, Matter, and Measurement

In April 2003, the US Pharmacopeia, a national organization that establishes quality standards for medications, reported a case in which a physician ordered “morphine [a powerful painkiller] 2–3 mg IV [intravenously] every 2–3 hours for pain.” A nurse misread the dose as “23 mg” and thus administered approximately 10 times the proper amount to an 8-year-old boy with a broken leg. The boy stopped breathing but was successfully resuscitated and left the hospital three days later.

Quantities and measurements are as important in our everyday lives as they are in medicine. The posted speed limits on roads and highways, such as 55 miles per hour (mph), are quantities we might encounter all the time. Both parts of a quantity, the amount (55) and the unit (mph), must be properly communicated to prevent potential problems. In chemistry, as in any technical endeavor, the proper expression of quantities is a necessary fundamental skill. As we begin our journey into chemistry, we will learn this skill so that errors—from homework mistakes to traffic tickets to more serious consequences—can be avoided.

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# 1.2: What is Chemistry?

**Learning Objectives**

1. Define chemistry in relation to other sciences.
2. Identify the general steps in the scientific method.

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 **1.2.1**). 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.

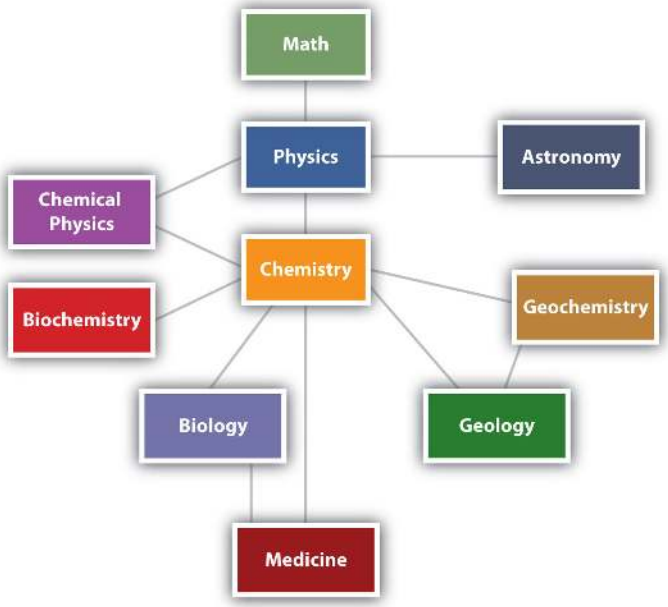



Figure **1.2.1**: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure **1.2.1** shows how many of the individual fields of science are related.

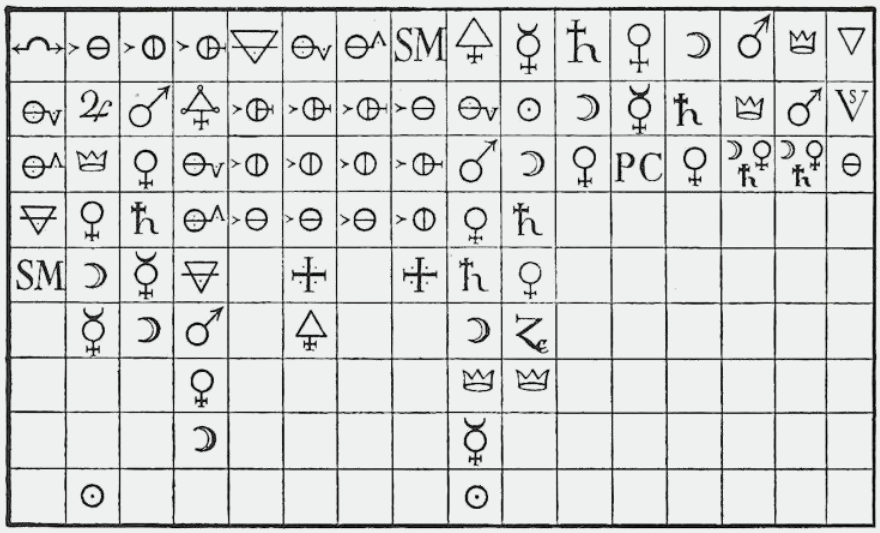
> *There are many other fields of science in addition to the ones listed here.*

**Alchemy**

As our understanding of the universe has changed over time, so has the practice of science. Chemistry in its modern form, based on principles that we consider valid today, was developed in the 1600s and 1700s. Before that, the study of matter was known as *alchemy* and was practiced mainly in China, Arabia, Egypt, and Europe.

Alchemy was a somewhat mystical and secretive approach to learning how to manipulate matter. Practitioners, called alchemists, thought that all matter was composed of different proportions of the four basic elements—fire, water, earth, and air—and believed that if you changed the relative proportions of these elements in a substance, you could change the substance. The long-standing attempts to “transmute” common metals into gold represented one goal of alchemy. Alchemy’s other major

goal was to synthesize the philosopher's stone, a material that could impart long life—even immortality. Alchemists used symbols to represent substances, some of which are shown in the accompanying figure. This was not done to better communicate ideas, as chemists do today, but to maintain the secrecy of alchemical knowledge, keeping others from sharing in it.




The first affinity table. Table of different relations observed in chemistry between different substances; Memoirs of the Royal Academy of Sciences, p. 202-212. Alchemists used symbols like these to represent substances.

In spite of this secrecy, in its time alchemy was respected as a serious, scholarly endeavor. Isaac Newton, the great mathematician and physicist, was also an alchemist.

## Exercise 1.2.1

Which fields of study are branches of science? Explain.

a. sculpture
b. astronomy

**Answer a**

Sculpture is not considered a science because it is not a study of some aspect of the natural universe.

**Answer b**

Astronomy is the study of stars and planets, which are part of the natural universe. Astronomy is therefore a field of science.

## Exercise 1.2.2

Which fields of study are branches of science?

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

**Answer**

a, b and c only

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. To find the answer to a question (for example, “Why do birds fly toward Earth’s equator during the cold months?”), a scientist goes through the following steps, which are also illustrated in Figure **1.2.2**:

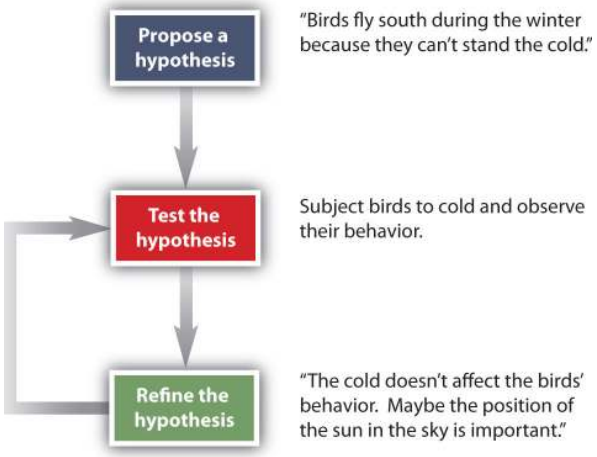



Figure **1.2.2**: The General Steps of the Scientific Method. After an observation is made or a question is identified, a hypothesis is made and experiments are designed to test the hypothesis.

The steps 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.

### 1.2.3 Exercise

Define science and chemistry.

**Answer**

Science is a process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Chemistry is the study of matter.

### 1.2.4 Exercise

Name the steps of the scientific method.

**Answer**

After identifying the problem or making an observation, propose a hypothesis, test the hypothesis, and refine the hypothesis, if necessary

## 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.

1. Based on what you know, which fields are branches of science?

    a. meteorology (the study of weather)
    b. astrophysics (the physics of planets and stars)
    c. economics (the study of money and monetary systems)
    d. astrology (the prediction of human events based on planetary and star positions)
    e. political science (the study of politics)

2. Based on what you know, which fields are a branches of science?

    a. history (the study of past events)
    b. ornithology (the study of birds)
    c. paleontology (the study of fossils)
    d. zoology (the study of animals)
    e. phrenology (using the shape of the head to determine personal characteristics)

3. Which of the following are examples of matter?

    a. a baby
    b. an idea
    c. the Empire State Building
    d. an emotion
    e. the air
    f. Alpha Centauri, the closest known star (excluding the sun) to our solar system

4. Which of the following are examples of matter?

    a. your textbook
    b. brain cells
    c. love
    d. a can of soda
    e. breakfast cereal

5. Suggest a name for the science that studies the physics of rocks and the earth.
6. Suggest a name for the study of the physics of living organisms.
7. Engineering is the practical application of scientific principles and discoveries to develop things that make our lives easier. Is medicine science or engineering? Justify your answer.
8. Based on the definition of engineering in Exercise 7, would building a bridge over a river or road be considered science or engineering? Justify your answer.
9. When someone says, “I have a theory that excess salt causes high blood pressure,” does that person really have a theory? If it is not a theory, what is it?
10. When a person says, “My hypothesis is that excess calcium in the diet causes kidney stones,” what does the person need to do to determine if the hypothesis is correct?
11. Some people argue that many scientists accept many scientific principles on faith. Using what you know about the scientific method, how might you argue against that assertion?
12. Most students take multiple English classes in school. Does the study of English use the scientific method?

## Answers

1.
    a. science
    b. science
    c. not science
    d. not science
    e. not science

2.
    a. not science
    b. science
    c. science
    d. science
    e. not science

3.
    a. matter
    b. not matter
    c. matter
    d. not matter
    e. matter
    f. matter

4.
    a. matter
    b. matter
    c. not matter
    d. matter
    e. matter

5. geophysics
6. biophysics
7. Medicine is probably closer to a field of engineering than a field of science, but this may be arguable. Ask your doctor.
8. Engineering
9. In scientific terms, this person has a hypothesis.
10. Conduct experiments to determine if kidney stones contain calcium.
11. Science is based on reproducible facts, not blind belief.
12. No.

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# 1.3: The Classification of Matter

**Learning Objectives**

- Use physical and chemical properties, including phase, to describe matter.
- Identify a sample of matter as an element, a compound, or a mixture.

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.

## Physical and Chemical Properties

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.



Figure **1.3.1**: (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 )

## Elements and Compounds

Any sample of matter that has the *same physical and chemical properties throughout* the sample is called a **substance**. There are two types of substances. A substance that cannot be broken down into chemically simpler components is called an **element**. Aluminum, which is used in soda cans and is represented by the symbol Al, is an element. A substance that can be broken down into chemically simpler components (because it consists of more than one element) is called a **compound**. Water is a compound composed of the elements hydrogen and oxygen and is described by the chemical formula, $H_2O$. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

> Sometimes the word *pure* is used to describe a substance, but this is not absolutely necessary. By definition, any single substance, element or compound is *pure*.

The smallest part of an element that maintains the identity of that element is called an **atom**. Atoms are extremely tiny; to make a line of iron atoms that is 1 inch long, you would need approximately 217 million iron atoms. The smallest part of a compound that maintains the identity of that compound is called a **molecule**. Molecules are composed of two or more different atoms that are attached together and behave as a unit. Scientists usually work with millions and millions of atoms and molecules at a time. When a

scientist is working with large numbers of atoms or molecules at a time, the scientist is studying the *macroscopic viewpoint* of the universe. However, scientists can also describe chemical events on the level of individual atoms or molecules, which is referred to as the *microscopic viewpoint*. We will see examples of both macroscopic and microscopic viewpoints throughout this book (Figure **1.3.2**).

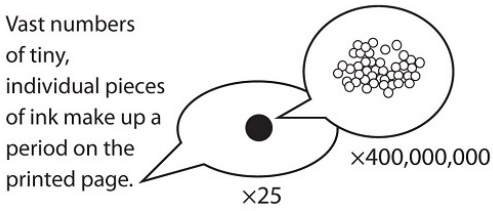



Figure **1.3.2**: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The ×25 and ×400,000,000 indicate the number of times the image is magnified.

## Mixtures

A material composed of two or more substances is a **mixture**. In a mixture, the individual substances maintain their chemical identities. Many mixtures are obvious combinations of two or more substances, such as a mixture of sand and water. Such mixtures are called **heterogeneous mixtures**. In some mixtures, the components are so intimately combined that they act like a single substance (even though they are not). Mixtures with a consistent or uniform composition throughout are called **homogeneous mixtures** (or solutions). For example, when sugar is dissolved in water to form a liquid solution, the individual properties of the components cannot be distinguished. Other examples or homogenous mixtures include solid solutions, like the metal alloy steel, and gaseous solutions, like air which is a mixture of mainly nitrogen and oxygen.

### Example 1.3.1

How would a chemist categorize each example of matter?

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

**Answer 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.

**Answer b**

Soil is composed of small pieces of a variety of materials, so it is a ***h**eterogeneous mixture*.

**Answer c**

Water is a *substance*; more specifically, because water is composed of hydrogen and oxygen, it is a *compound*.

**Answer d**

Oxygen, a *substance*, is an *element*.

### Exercise 1.3.1

How would a chemist categorize each example of matter?

a. breakfast coffee
b. hydrogen
c. an egg

**Answer a**

homogeneous mixture or solution

**Answer b**

element

**Answer c**

heterogeneous mixture

## Phases or Physical States of Matter

All matter can be further classified by one of three physical **states** or **phases**, solid, liquid or gas. 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.

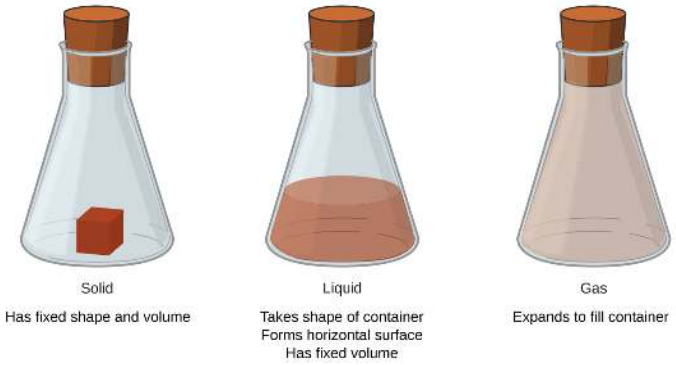



Figure **1.3.3**: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

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) (Figure **1.3.2**).



Figure **1.3.5**: Boiling Water. When liquid water boils to make gaseous water, it undergoes a phase change. (CC BY-SA 3.0 Unported; Markus Schweiss via Wikipedia)

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 **phase change**, a physical process in which a substance changes from one phase to another (Figure **1.3.5**). Phase changes are identified by particular names depending on what phases are involved, as summarized in Table **1.3.1**.

Table **1.3.1**: Phase 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 |

Figure **1.3.3** illustrates the relationships between the different ways matter can be classified.

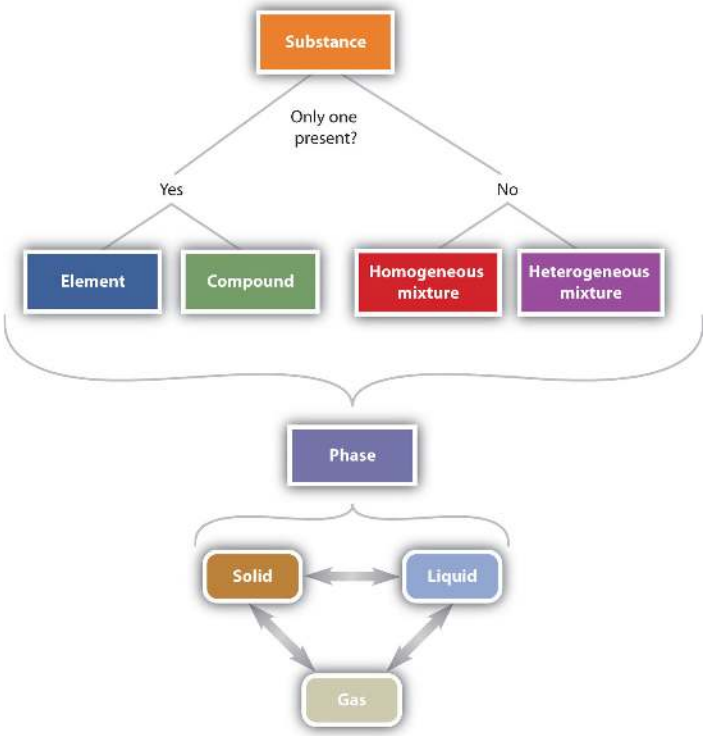



Figure **1.3.6**: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.

## Concept Review Exercises

1. Explain the differences between the physical properties of matter and the chemical properties of matter.
2. What is the difference between a heterogeneous mixture and a homogeneous mixture? Give an example of each.
3. Give at least two examples of a phase change and state the phases involved in each.

## Answers

1. Physical properties describe the existence of matter, and chemical properties describe how substances change into other substances.
2. A heterogeneous mixture is obviously a mixture, such as dirt; a homogeneous mixture behaves like a single substance, such as saltwater.
3. solid to liquid (melting) and liquid to gas (boiling) (answers will vary)

## Key Takeaways

- Matter can be described with both physical properties and chemical properties.
- Matter can be identified as an element, a compound, or a mixture.

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# 1.4: Measurements

**Learning Objectives**

- Express quantities properly using a number and a unit.

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 **1.4.1**); the nurse is also measuring.



Figure **1.4.1**: 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. The next two sections examine the rules for expressing numbers.

**Exercise 1.4.1**

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

**Answer a**

The number is one, and the unit is dozen.

**Answer b**

The number is 2.54, and the unit is centimeter.

**Answer c**

The number 1 is implied because the quantity is only *a* box. The unit is box of pencils.

**Answer 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 1.4.2

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

### ? Exercise 1.4.2

What are the two necessary parts of a quantity?

**Answer**

The two necessary parts are the number and the unit.

## Key Takeaway

- Identify a quantity properly with a number and a unit.

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# 1.5: Expressing Numbers - Scientific Notation

**Learning Objectives**

- Express a large number or a small number in scientific notation.
- Convert a number in scientific notation to standard conventional form.

The instructions for making a pot of coffee specified 3 scoops (rather than 12,000 grounds) because any measurement is expressed more efficiently with units that are appropriate in size. In science, however, we often must deal with quantities that are extremely small or incredibly large. For example, you may have 5,000,000,000,000 red blood cells in a liter of blood, and the diameter of an iron atom is 0.000000014 inches. Numbers with many zeros can be cumbersome to work with, so scientists use scientific notation.

**Scientific notation** is a system for expressing very large or very small numbers in a compact manner. It uses the idea that such numbers can be rewritten as a simple number multiplied by 10 raised to a certain exponent, or power.

Let us look first at very large numbers. Suppose a spacecraft is 1,500,000 miles from Mars. The number 1,500,000 can be thought of as follows:

$$1.5 \times \underbrace{1{,}000{,}000}_{\underbrace{10 \times 10 \times 10 \times 10 \times 10 \times 10}_{10^6}} = 1.5 \times 10^6$$

That is, 1,500,000 is the same as 1.5 times 1 million, and 1 million is 10 × 10 × 10 × 10 × 10 × 10, or $10^6$ (which is read as "ten to the sixth power"). Therefore, 1,500,000 can be rewritten as 1.5 times $10^6$, or $1.5 \times 10^6$. The distance of the spacecraft from Mars can therefore be expressed as $1.5 \times 10^6$ miles.

Recall that:

- $10^0 = 1$
- $10^1 = 10$
- $10^2 = 100$
- $10^3 = 1{,}000$
- $10^4 = 10{,}000$
- and so forth

The standard convention for expressing numbers in scientific notation is to write a single *nonzero* first digit, a decimal point, and the rest of the digits, excluding any trailing zeros (see rules for significant figures in the next section for more details on what to exclude). This number is followed by a multiplication sign and then by 10 raised to the power necessary to reproduce the original number. For example, although 1,500,000 can also be written as $15. \times 10^5$ (which would be 15. × 100,000), the convention is to have only one digit before the decimal point. How do we know to what power 10 is raised? The power is the number of places you have to move the decimal point to the *left* to place it after the first digit, so that the number being multiplied is *between 1 and 10*:

$$1{,}500{,}000 = 1.5 \times 10^6$$

**Example 1.5.1: Scientific Notation**

Express each number in scientific notation.

a. 67,000,000,000
b. 1,689
c. 12.6

**Answer a**

Moving the decimal point 10 places to the left gives $6.7 \times 10^{10}$.

**Answer b**

The decimal point is assumed to be at the end of the number, so moving it three places to the left gives $1.689 \times 10^3$.

**Answer c**

In this case, we need to move the decimal point only one place to the left, which yields $1.26 \times 10^1$.

**? Exercise 1.5.1**

Express each number in scientific notation.

a. 1,492
b. 102,000,000
c. 101,325

**Answer a**

Moving the decimal point 3 places to the left gives $1.492 \times 10^3$.

**Answer b**

The decimal point is assumed to be at the end of the number, so moving it 8 places to the left gives $1.02 \times 10^8$.

**Answer c**

Moving the decimal point 5 places to the left yields $1.01325 \times 10^5$.

To change a number in **scientific notation** to **standard form**, we reverse the process, moving the decimal point to the right. Add zeros to the end of the number being converted, if necessary, to produce a number of the proper magnitude. Lastly, we drop the number 10 and its power.

$$1.5 \times 10^6 = 1.500000 = 1{,}500{,}000$$

**✓ Example 1.5.2**

Express each number in standard, or conventional notation.

a. $5.27 \times 10^4$
b. $1.0008 \times 10^6$

**Answer a**

Moving the decimal four places to the right and adding zeros give 52,700.

**Answer b**

Moving the decimal six places to the right and adding zeros give 1,000,800.

**✓ Exercise 1.5.2**

Express each number in standard, or conventional notation.

a. $6.98 \times 10^8$
b. $1.005 \times 10^2$

**Answer a**

Moving the decimal point eight places to the right and adding zeros give 698,000,000.

**Answer b**

Moving the decimal point two places to the right gives 100.5

We can also use scientific notation to express numbers whose magnitudes are less than 1. For example, the quantity 0.006 centimeters can be expressed as follows:

$$6 \times \underbrace{\frac{1}{1{,}000}}_{\underbrace{\frac{1}{10} \times \frac{1}{10} \times \frac{1}{10}}_{10^{-3}}} = 6 \times 10^{-3}$$

That is, 0.006 centimeters is the same as 6 *divided by* one thousand, which is the same as 6 *divided* by 10 x 10 x 10 or 6 *times* $10^{-3}$ (which is read as "ten to the negative third power"). Therefore, 0.006 centimeters can be rewritten as 6 times $10^{-3}$, or $6 \times 10^{-3}$ centimeters.

Recall that:

- $10^{-1} = 1/10$
- $10^{-2} = 1/100$
- $10^{-3} = 1/1{,}000$
- $10^{-4} = 1/10{,}000$
- $10^{-5} = 1/100{,}000$
- and so forth

We use a negative number as the power to indicate the number of places we have to move the decimal point to the right to make it follow the first nonzero digit so that the number is between 1 and 10. This is illustrated as follows:

$$0.006 = 6 \times 10^{-3}$$

**Note:**

In writing scientific notations, the convention is to have only one digit before the decimal point.

- Numbers that are greater than one have a positive power in scientific notation. If the decimal point is moved to the left n places, the power (n) of 10 is positive. $1{,}500{,}000 = 1.5 \times 10^{6}$
- Numbers that are less than one have a negative power in scientific notation. If the decimal point is moved to the right n places, the power (n) of 10 is negative. $0.006 = 6 \times 10^{-3}$

**Example 1.5.3**

Express each number in scientific notation.

a. 0.000006567
b. −0.0004004
c. 0.000000000000123

**Answer a**

Move the decimal point six places to the right to get $6.567 \times 10^{-6}$.

**Answer b**

Move the decimal point four places to the right to get $-4.004 \times 10^{-4}$. The negative sign on the number itself does not affect how we apply the rules of scientific notation.

**Answer c**

Move the decimal point 13 places to the right to get $1.23 \times 10^{-13}$.

**Exercise 1.5.3**

Express each number in scientific notation.

a. 0.000355
b. 0.314159
c. −0.051204

**Answer a**

Moving the decimal point four places to the right gives $3.55 \times 10^{-4}$.

**Answer b**

Moving the decimal point one place to the right gives $3.14159 \times 10^{-1}$.

**Answer c**

Moving the decimal point one place to the right gives $-5.1204 \times 10^{-2}$.

As with numbers with positive powers of 10, when changing from **scientific** notation to **standard or conventional** format, we reverse the process.

$$6 \times 10^{-3} = .006 = 0.006$$

**Note**

Changing a number in scientific notation to standard form:

- If the scientific notation has a positive power, the standard number is greater than one. Example: $8 \times 10^{4} = 80{,}000$
- If the scientific notation has a negative power, then the standard number is less than one. Example: $8 \times 10^{-2} = 0.08$

**Example 1.5.4**

Change the number in scientific notation to standard form.

a. $6.22 \times 10^{-2}$
b. $9.9 \times 10^{-9}$

**Answer a**

0.0622

**Answer b**

0.0000000099

**Exercise 1.5.4**

Change the number in scientific notation to standard form.

a. $9.98 \times 10^{-5}$
b. $5.109 \times 10^{-8}$

**Answer a**

0.0000998

**Answer b**

0.00000005109

Although calculators can show 8 to 10 digits in their display windows, that is not always enough when working with very large or very small numbers. For this reason, many calculators are designed to handle scientific notation. The method for entering scientific notation differs for each calculator model, so take the time to learn how to do it properly on your calculator, *asking your instructor for assistance if necessary*. If you do not learn to enter scientific notation into your calculator properly, you will not get the correct final answer when performing a calculation.

**? Exercise 1.5.1**

Why it is easier to use scientific notation to express very large or very small numbers?

**Answer**

Scientific notation is more convenient than listing a large number of zeros.

**? Exercise 1.5.2**

What is the relationship between how many places a decimal point moves and the power of 10 used in changing a conventional number into scientific notation?

**Answer**

The number of places the decimal point moves equals the power of 10. The power of 10 is positive if the decimal point moves to the left and negative if the decimal point moves to the right.

## Key Takeaway

- Large or small numbers are expressed in scientific notation, which use powers of 10.

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# 1.6: Expressing Numbers - Significant Figures

**Learning Objectives**

- Understand the importance of significant figures in measured numbers.
- Identify the number of significant figures in a reported value.
- Use significant figures correctly in arithmetical operations.

Scientists have established certain conventions for communicating the degree of **precision** of a measurement, which is dependent on the measuring device used. 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*. 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. However, you can *estimate* one past the smallest marking, in this case the millimeter, to the next decimal place in the measurement (Figure 1.6.1).

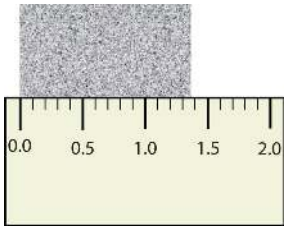



Figure 1.6.1: Measuring an Object to the Correct Number of Digits. How many digits should be reported for the length of this object?

The concept of **significant figures** takes this limitation 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 report any digits after the first uncertain one, so it is the last 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.

> *"Sig figs" is a common abbreviation for 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:

1. All nonzero digits are significant. In 1,357 mm, all the digits are significant.
2. *Sandwiched (or embedded) zeros*, those between significant digits, are significant. Thus, 405 g has *three* significant figures.
3. *Leading zeros*, which are zeros at the beginning of a decimal number less than 1, are not significant. In 0.000458 mL, the first four digits are leading zeros and are not significant. The zeros serve only to put the digits 4, 5, and 8 in the correct decimal positions. This number has three significant figures.
4. *Trailing zeros*, which are zeros at the end of a number, are significant only if the number has a decimal point. Thus, in 1,500 m, the two trailing zeros are not significant because the number is written without a decimal point; the number has two significant

figures. However, in 1,500.00 m, all six digits are significant because the number has a decimal point.

### Example 1.6.1

How many significant figures does each number have?

a. 6,798,000
b. 6,000,798
c. 6,000,798.00
d. 0.0006798

**Answer a**

four (by rules 1 and 4)

**Answer b**

seven (by rules 1 and 2)

**Answer c**

nine (by rules 1, 2, and 4)

**Answer d**

four (by rules 1 and 3)

### Exercise 1.6.1

How many significant figures does each number have?

a. 2.1828
b. 0.005505
c. 55,050
d. 5
e. 500

**Answer a**

five

**Answer b**

four

**Answer c**

four

**Answer d**

one

**Answer e**

one

## Rounding off numbers

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

Table 1.5.1: Rounding examples

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

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

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

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

## Combining Numbers

For **addition or subtraction**, the rule is to stack all the numbers with their decimal points aligned and then limit (round to) the answer's significant figures to the rightmost column for which all the numbers have significant figures. Consider the following:

```
    56.789
+   102.2
+ 1,300.099
= 1,459.088
      ↑ Limit to this column
```

The arrow points to the rightmost column in which all the numbers have significant figures—in this case, the tenths place. Therefore, we will limit our final answer to the tenths place. Is our final answer therefore 1,459.0? No, because when we drop digits from the end of a number, we also have to round the number. Notice that the first dropped digit, in the hundredths place, is 8. This suggests that the answer is actually closer to 1,459.1 than it is to 1,459.0, so we need to round up to **1,459.1**. The standard rules for rounding numbers are simple: If the first dropped digit is 5 or higher, round up. If the first dropped digit is lower than 5, do not round up.

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:

```
38.65 × 105.93 = 4,094.1945
4 sig figs  5 sig figs  reduce to 4 sig figs
```

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

Scientific notation provides a way of communicating significant figures without ambiguity. You simply include all the significant figures in the leading number. For example, the number 4,000 has one significant figure and should be written as the number $4 \times 10^4$. The number 450 has two significant figures and would be written in scientific notation as $4.5 \times 10^2$, whereas 450.0 has four significant figures and would be written as $4.500 \times 10^2$. In scientific notation, all reported digits are significant.

### Example 1.6.2

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
c. 1,027 + 610.0 + 363.06

**Answer a**

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 hundredths place) is greater than 5, we round up to 2,085.6, which in scientific notation is $2.0856 \times 10^3$.

**Answer b**

The calculator gives 1,125 as the answer, but we limit it to three significant figures and convert into scientific notation: $1.13 \times 10^3$.

**Answer c**

The calculator gives 2,000.06 as the answer, but because 1,027 has its farthest-right significant figure in the ones column, our answer must be limited to the ones position: 2,000 which in scientific notation is $2.000 \times 10^3$.

### Exercise 1.6.2

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**

$1437 = 1.437 \times 10^3$

**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.

### Exercise 1.6.1

Explain why the concept of significant figures is important in scientific measurements.

**Answer**

Significant figures represent all the known digits of a measurement plus the first estimated one. It gives information about how precise the measuring device and measurement is.

**? Exercise 1.6.2**

State the rules for determining the significant figures in a measurement.

**Answer**

All nonzero digits are significant; zeros between nonzero digits are significant; zeros at the end of a nondecimal number or the beginning of a decimal number are not significant; zeros at the end of a decimal number are significant.

**? Exercise 1.6.3**

When do you round a number up, and when do you not round a number up?

**Answer**

Round up only if the first digit dropped is 5 or higher.

## Key Takeaways

- Significant figures properly report the number of measured and estimated digits in a measurement.
- The rule in multiplication and division is that the final answer should have the same number of significant figures as there are in the value with the fewest significant figures.
- The rule in addition and subtraction is that the final answer should have the same number of decimal places as the term with the fewest decimal places.

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# 1.7: The International System of Units

**Learning Objectives**

- Recognize the SI base units and explain the system of prefixes used with them.
- Define and calculate density.

People who live in the United States measure weight in pounds, height in feet and inches, and a car's speed in miles per hour. In contrast, chemistry and other branches of science use the International System of Units (also known as **SI** after *Système Internationale d'Unités*), which was established so that scientists around the world could communicate efficiently with each other. Many countries have also adopted SI units for everyday use as well. The United States is one of the few countries that has not.

## Base SI Units

**Base (or basic) units**, are the fundamental units of SI. There are seven base units, which are listed in Table **1.7.1**, Chemistry uses five of the base units: the mole for amount, the kilogram for mass, the meter for length, the second for time, and the kelvin for temperature. The degree Celsius (°C) is also commonly used for temperature. The numerical relationship between kelvins and degrees Celsius is as follows:

$$K = °C + 273 \tag{1.7.1}$$

The United States uses the English (sometimes called Imperial) system of units for many quantities. Inches, feet, miles, gallons, pounds, and so forth, are all units connected with the English system of units. There have been many mistakes due to the improper conversion of units between the SI and English systems.

Table **1.7.1**: The Seven Base SI Units

| Property | Unit | Abbreviation |
|---|---|---|
| length | meter | m |
| mass | kilogram | kg |
| time | second | s |
| amount | mole | mol |
| temperature | kelvin | K |
| electrical current | ampere | amp |
| luminous intensity | candela | cd |

The size of each base unit is defined by international convention. For example, the *kilogram* is defined as the quantity of mass of a special metal cylinder kept in a vault in France (Figure **1.7.1**). The other base units have similar definitions and standards. The sizes of the base units are not always convenient for all measurements. For example, a meter is a rather large unit for describing the width of something as narrow as human hair. Instead of reporting the diameter of hair as 0.00012 m or as $1.2 \times 10^{-4}$ m using scientific notation as discussed in section 1.4, SI also provides a series of **prefixes** that can be attached to the units, creating units that are larger or smaller by powers of 10.

Common prefixes and their multiplicative factors are listed in Table **1.7.2**. (Perhaps you have already noticed that the base unit *kilogram* is a combination of a prefix, kilo- meaning 1,000 ×, and a unit of mass, the gram.) Some prefixes create a multiple of the original unit: 1 kilogram equals 1,000 grams, and 1 megameter equals 1,000,000 meters. Other prefixes create a fraction of the original unit. Thus, 1 centimeter equals 1/100 of a meter, 1 millimeter equals 1/1,000 of a meter, 1 microgram equals 1/1,000,000 of a gram, and so forth.

Table **1.7.2**: Prefixes Used with SI Units

| Prefix | Abbreviation | Multiplicative Factor | Multiplicative Factor in Scientific Notation |
|---|---|---|---|
| giga- | G | 1,000,000,000 × | $10^{9}$ × |
| mega- | M | 1,000,000 × | $10^{6}$ × |
| kilo- | k | 1,000 × | $10^{3}$ × |
| deca- | D | 10 × | $10^{1}$ × |
| deci- | d | 1/10 × | $10^{-1}$ × |
| centi- | c | 1/100 × | $10^{-2}$ × |
| milli- | m | 1/1,000 × | $10^{-3}$ × |
| micro- | μ* | 1/1,000,000 × | $10^{-6}$ × |
| nano- | n | 1/1,000,000,000 × | $10^{-9}$ × |

*The letter μ is the Greek lowercase letter for *m* and is called “mu,” which is pronounced “myoo.”

Both SI units and prefixes have abbreviations, and the combination of a prefix abbreviation with a base unit abbreviation gives the abbreviation for the modified unit. For example, kg is the abbreviation for kilogram. We will be using these abbreviations throughout this book.



Figure **1.7.1**: The Kilogram. The standard for the kilogram is a platinum-iridium cylinder kept in a special vault in France. Source: Photo reproduced by permission of the Bureau International des Poids et Mesures, who retain full internationally protected copyright.

### 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 $m/s^2$. 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).

## Derived SI Units

**Derived units** are combinations of SI base units. Units can be multiplied and divided, just as numbers can be multiplied and divided. For example, the area of a square having a side of 2 cm is 2 cm × 2 cm, or 4 $cm^2$ (read as “four centimeters squared” or “four square centimeters”). Notice that we have squared a length unit, the centimeter, to get a derived unit for area, the square centimeter.

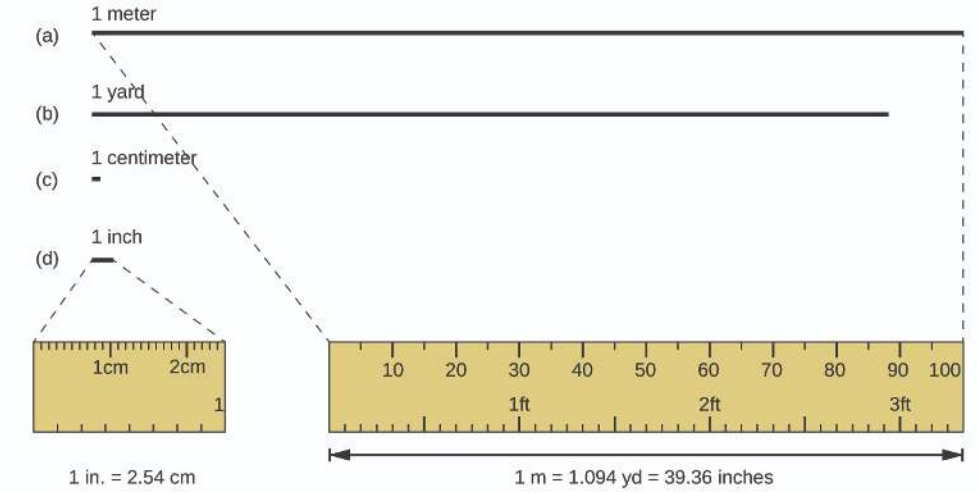



Figure 1.7.2: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

Volume is an important quantity that uses a derived unit. **Volume** is the amount of space that a given substance occupies and is defined geometrically as length × width × height. Each distance can be expressed using the meter unit, so volume has the derived unit m × m × m, or $m^3$ (read as “meters cubed” or “cubic meters”). A cubic meter is a rather large volume, so scientists typically express volumes in terms of 1/1,000 of a cubic meter. This unit has its own name—the liter (L). A liter is a little larger than 1 US quart in volume. Below are approximate equivalents for some of the units used in chemistry.

Approximate Equivalents to Some SI Units

- 1 m ≈ 39.36 in. ≈ 3.28 ft ≈ 1.09 yd
- 1 in. ≈ 2.54 cm
- 1 km ≈ 0.62 mi
- 1 kg ≈ 2.20 lb
- 1 lb ≈ 454 g
- 1 L ≈ 1.06 qt
- 1 qt ≈ 0.946 L

As shown in Figure 1.7.3, a liter is also 1,000 $cm^3$. By definition, there are 1,000 mL in 1 L, so 1 milliliter and 1 cubic centimeter represent the same volume.

$$1\ mL = 1\ cm^3 \tag{1.7.2}$$

### Example 1.7.1

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

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

**Answer a**

The abbreviation for a kiloliter is kL. Because kilo means “1,000 ×,” 1 kL equals 1,000 L.

**Answer b**

The abbreviation for microsecond is µs. Micro implies 1/1,000,000th of a unit, so 1 µs equals 0.000001 s.

**Answer c**

The abbreviation for decimeter is dm. Deci means 1/10th, so 1 dm equals 0.1 m.

**Answer d**

The abbreviation for nanogram is ng and equals 0.000000001 g.

## ? Exercise 1.7.1

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 (1,000 m)

**Answer b**

mg (0.001 g)

**Answer c**

ns (0.000000001 s)

**Answer d**

cL (0.01L)

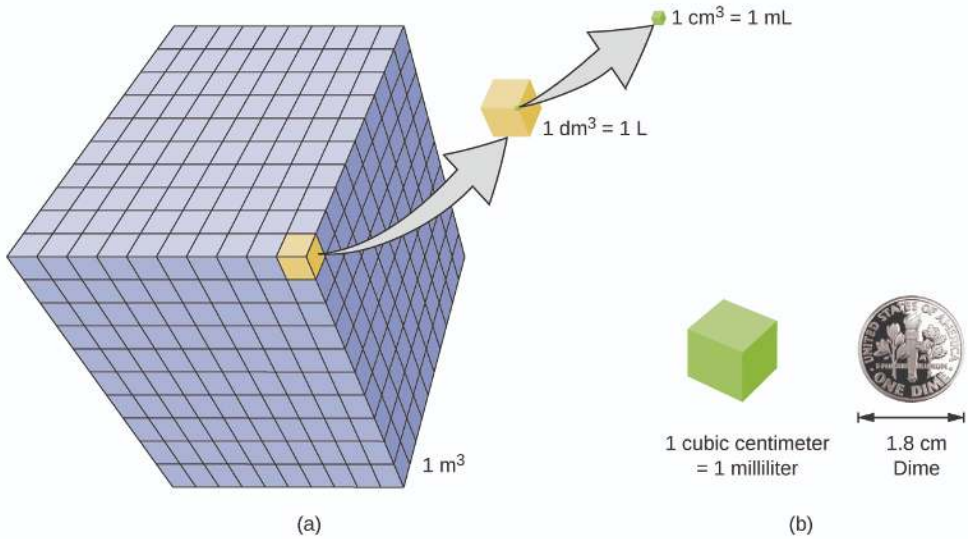



Figure **1.7.3**: Units of Volume. (a) The relative volumes are shown for cubes of 1 $m^3$, 1 $dm^3$ (1 L), and 1 $cm^3$ (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter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

**Energy**, another important quantity in chemistry, is the ability to perform work, such as moving a box of books from one side of a room to the other side. It has a derived unit of kg•$m^2/s^2$. (The dot between the kg and m units implies the units are multiplied together.) Because this combination is cumbersome, this collection of units is redefined as a **joule** (J). An older unit of energy, but

likely more familiar to you, the calorie (cal), is also widely used. There are 4.184 J in 1 cal. Energy changes occur during all chemical processes and will be discussed in a later chapter.

### To Your Health: Energy and Food

The food in our diet provides the energy our bodies need to function properly. The energy contained in food could be expressed in joules or calories, which are the conventional units for energy, but the food industry prefers to use the kilocalorie and refers to it as the Calorie (with a capital C). The average daily energy requirement of an adult is about 2,000–2,500 Calories, which is 2,000,000–2,500,000 calories (with a lowercase c).

If we expend the same amount of energy that our food provides, our body weight remains stable. If we ingest more Calories from food than we expend, however, our bodies store the extra energy in high-energy-density compounds, such as fat, and we gain weight. On the other hand, if we expend more energy than we ingest, we lose weight. Other factors affect our weight as well—genetic, metabolic, behavioral, environmental, cultural factors—but dietary habits are among the most important.

In 2008 the US Centers for Disease Control and Prevention issued a report stating that 73% of Americans were either overweight or obese. More alarmingly, the report also noted that 19% of children aged 6–11 and 18% of adolescents aged 12–19 were overweight—numbers that had tripled over the preceding two decades. Two major reasons for this increase are excessive calorie consumption (especially in the form of high-fat foods) and reduced physical activity. Partly because of that report, many restaurants and food companies are working to reduce the amounts of fat in foods and provide consumers with more healthy food options.

**Density** is defined as the mass of an object divided by its volume; it describes the amount of matter contained in a given amount of space.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.7.3}$$

Thus, the units of density are the units of mass divided by the units of volume: g/cm$^3$ or g/mL (for solids and liquids), g/L (for gases), kg/m$^3$, and so forth. For example, the density of water is about 1.00 g/cm$^3$, while the density of mercury is 13.6 g/mL. (Remember that 1 mL equals 1 cm$^3$.) Mercury is over 13 times as dense as water, meaning that it contains over 13 times the amount of matter in the same amount of space. The density of air at room temperature is about 1.3 g/L. Table 1.6.3 shows the densities of some common substances.

Table **1.7.2**: Densities of Common Substances

| Solids | Liquids | Gases (at 25 °C and 1 atm) |
|---|---|---|
| ice (at 0 °C) 0.92 g/cm$^3$ | water 1.0 g/cm$^3$ | dry air 1.20 g/L |
| oak (wood) 0.60–0.90 g/cm$^3$ | ethanol 0.79 g/cm$^3$ | oxygen 1.31 g/L |
| iron 7.9 g/cm$^3$ | acetone 0.79 g/cm$^3$ | nitrogen 1.14 g/L |
| copper 9.0 g/cm$^3$ | glycerin 1.26 g/cm$^3$ | carbon dioxide 1.80 g/L |
| lead 11.3 g/cm$^3$ | olive oil 0.92 g/cm$^3$ | helium 0.16 g/L |
| silver 10.5 g/cm$^3$ | gasoline 0.70–0.77 g/cm$^3$ | neon 0.83 g/L |
| gold 19.3 g/cm$^3$ | mercury 13.6 g/cm$^3$ | radon 9.1 g/L |

### Example 1.7.2: Density of Bone

What is the density of a section of bone if a 25.3 cm$^3$ sample has a mass of 27.8 g?

#### Solution

Because density is defined as the mass of an object divided by its volume, we can set up the following relationship:

$$\begin{aligned} \text{density} &= \frac{mass}{volume} \\ &= \frac{27.8\ g}{25.3\ cm^3} \\ &= 1.10\ g/cm^3 \end{aligned}$$

Note that we have limited our final answer to three significant figures.

**? Exercise 1.7.2: Density of Oxygen**

What is the density of oxygen gas if a 15.0 L sample has a mass of 21.7 g?

**Answer**

1.45 g/L

Density can be used to convert between the mass and the volume of a substance. This will be discussed in the next section.

## Concept Review Exercises

1. What is the difference between a base unit and a derived unit? Give two examples of each type of unit.
2. Do units follow the same mathematical rules as numbers do? Give an example to support your answer.
3. What is density?

## Answers

1. Base units are the seven fundamental units of SI; derived units are constructed by making combinations of the base units; Two examples of base units: kilograms and meters (answers will vary); Two examples of derived units: grams per milliliter and joules (answers will vary).
2. yes; $\mathbf{mL} \times \frac{\mathbf{g}}{\mathbf{mL}} = \mathbf{g}$ (answers will vary)
3. Density is defined as the mass of an object divided by its volume

## Key Takeaways

- Recognize the SI base units and derived units.
- Combining prefixes with base units creates new units of larger or smaller sizes.

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# 1.8: Converting Units

**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, 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:

$$\frac{3.55}{1} \times \frac{100\ \text{cm}}{1} = 355\ \text{cm} \tag{1.8.1}$$

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 1.8.1), 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 1.8.1 shows a **concept map** for constructing a proper conversion.

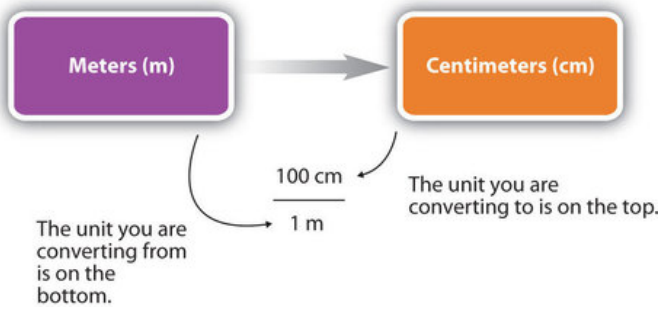



Figure 1.8.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Meters converted to centimeters. A fraction showing 100 cm over 1 m. The unit you convert to is on top, and the unit you convert from is on bottom.

## 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 1.8.1

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

**Solution**

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

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

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



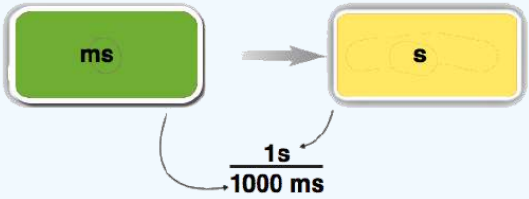

$$4.7 \cancel{L} \times \frac{1,000 \text{ mL}}{1 \cancel{L}} = 4,700 \text{ mL}$$

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

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

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

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




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

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

**? Exercise 1.8.1**

Perform each conversion.

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

**Answer a**

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

**Answer b**

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

## Conversion Factors From Different Units

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

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

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

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

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

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

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

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

### Example 1.8.2: 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 1.8.2

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.

### Looking Closer: Density and the Body

The densities of many components and products of the body have a bearing on our health.

**Bones.** Bone density is important because bone tissue of lower-than-normal density is mechanically weaker and susceptible to breaking. The density of bone is, in part, related to the amount of calcium in one's diet; people who have a diet deficient in calcium, which is an important component of bones, tend to have weaker bones. Dietary supplements or adding dairy products to the diet seems to help strengthen bones. As a group, women experience a decrease in bone density as they age. It has been estimated that fully half of women over age 50 suffer from excessive bone loss, a condition known as osteoporosis. Exact bone densities vary within the body, but for a healthy 30-year-old female, it is about 0.95–1.05 g/cm$^3$. Osteoporosis is diagnosed if the bone density is below 0.6–0.7 g/cm$^3$.

**Urine.** The density of urine can be affected by a variety of medical conditions. Sufferers of diabetes produce an abnormally large volume of urine with a relatively low density. In another form of diabetes, called diabetes mellitus, there is excess glucose dissolved in the urine, so that the density of urine is abnormally high. The density of urine may also be abnormally high because of excess protein in the urine, which can be caused by congestive heart failure or certain renal (kidney) problems. Thus, a urine density test can provide clues to various kinds of health problems. The density of urine is commonly expressed as a specific gravity, which is a unitless quantity defined as

$$\frac{\text{density of some material}}{\text{density of water}}$$

Normal values for the specific gravity of urine range from 1.002 to 1.028.

**Body Fat.** The overall density of the body is one indicator of a person's total body fat. Fat is less dense than muscle and other tissues, so as it accumulates, the overall density of the body decreases. Measurements of a person's weight and volume provide the overall body density, which can then be correlated to the percentage of body fat. (The body's volume can be measured by immersion in a large tank of water. The amount of water displaced is equal to the volume of the body.)

## Problem Solving With Multiple Conversions

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

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

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

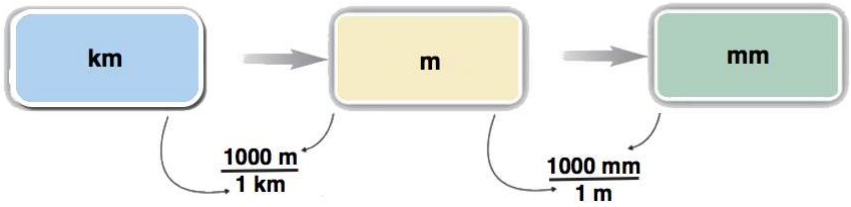
Then we take the result (54,700 m) and convert it to millimeters, remembering that there are $1,000 \text{ mm}$ for every $1 \text{ m}$:

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

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

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

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.

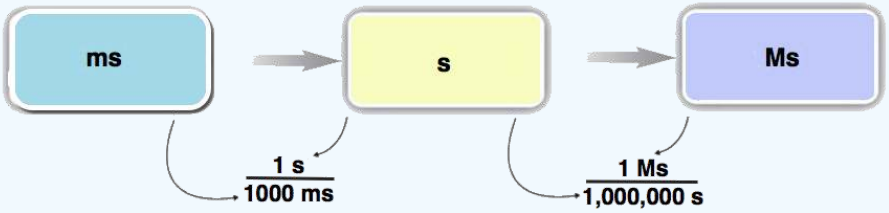
## Example 1.8.3

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




### 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 1.8.3

Convert 43.007 mg to kilograms in one multistep calculation.

**Answer**

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

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

.

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

## Career Focus: Pharmacist

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

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

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

## Key Takeaway

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

## Concept Review Exercises

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

## Answers

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




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

---

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# 1.9: Dosage Calculations

**Learning Objectives**

- Calculate drug dosages using conversion factors.

## To Your Health: Dosages

A medicine can be more harmful than helpful if it is not taken in the proper dosage. A dosage (or dose) is the specific amount of a medicine that is known to be therapeutic for an ailment in a patient of a certain size. Dosages of the active ingredient in medications are usually described by units of mass, typically grams or milligrams, and generally are equated with a number of capsules or teaspoonfuls to be swallowed or injected. The amount of the active ingredient in a medicine is carefully controlled so that the proper number of pills or spoonfuls contains the proper dose.

Most drugs must be taken in just the right amount. If too little is taken, the desired effects will not occur (or will not occur fast enough for comfort); if too much is taken, there may be potential side effects that are worse than the original ailment. Some drugs are available in multiple dosages. For example, tablets of the medication levothyroxine sodium, a synthetic thyroid hormone for those suffering from decreased thyroid gland function, are available in 11 different doses, ranging from 25 micrograms (µg) to 300 µg. It is a doctor's responsibility to prescribe the correct dosage for a patient, and it is a pharmacist's responsibility to provide the patient with the correct medicine at the dosage prescribed. Thus, proper quantities—which are expressed using numbers and their associated units—are crucial for keeping us healthy.

## Effects are dose-dependent

Chemicals are the most common things for which doses are measured, but there are others, such as radiation exposure. For humans, most doses of micronutrients and medications are measured in milligrams (mg), but some are measured in micrograms because of their potency. Nonmedicinal poisons span the measurement scale; some poisons are so dangerous that a single microgram of it could be deadly, whereas other substances take much more. For example, even water is toxic when consumed in large enough quantities.

Dosage (the size of each dose) determines the strength and duration of the health benefits of nutrients, and also of the therapeutic effects of medical treatments. Dosage also determines the severity of adverse effects of treatments and toxins.

Duration of exposure, that is, the period of time over which the dose was received (all at once or gradually) also determines its effects (the body may build tolerance to gradual exposure to a drug, while a large immediate dose could be deadly).

The route by which a dose is exposed to, may affect the outcome, because some medications have different effects depending on whether they are inhaled, ingested, taken transdermally, injected, or inserted.

The dosage, route, concentration, and division over time may all be critical considerations in the administering of drugs, or in responding to exposure to a toxin. In nutrition, the route is usually a given, as nutrients are generally eaten; while dosage and the frequency of ingestion of nutrients are very important variables in preventing disease and promoting overall health.

## Calculation of dose

Calculating drug dosages for humans based on the doses used in animal studies can be based on weight (e.g., mg/kg) or surface area (e.g., mg/m$^2$) based on weight. Drug dosage calculation is required if the physician's order is different from what is available.

**Example 1.9.1**

a. A physician ordered 100 mg of Demerol. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?

b. The doctor's order is 1.2 g of Folic Acid. Folic Acid is available as 800 mg per tablet. How many tablets should be taken?

**Solution**

a. We start with the given, 100 mg. We want to change the unit from *mg* to *tablets*. There are 50 mg in 1 tablet (Remember that *per* tablet means *one* tablet. From this relationship, we can construct the conversion factor. We use the conversion factor that

will cancel out the original unit, *mg*, and introduce the unit we are converting to, which is *tablet*.

$$100 \cancel{\text{mg}} \times \frac{1 \text{ tablet}}{50 \cancel{\text{mg}}} = 2 \text{ tablets}$$

Hence, the nurse should administer 2 tablets.

b. We start with the given, 1.2 g and we want to change *grams* to number of *tablets*. First, we convert *1.2 g* to *mg* and then convert *mg to tablets*. We need a conversion factor for each step.

$$1.2 \cancel{\text{g}} \times \frac{1{,}000 \cancel{\text{mg}}}{1 \cancel{\text{g}}} \times \frac{1 \text{ tablet}}{800 \cancel{\text{mg}}} = 1.5 \text{ tablets}$$

Hence, 1.5 tablets should be taken.

## ? Exercise 1.9.1

Calculate each of the following.

a. The physician ordered 20 mg of Valium. Valium is available as 10 mg per tablet. How many tablets should the nurse administer?
b. The doctor's order is 1 g of Calcium. What is on hand is Calcium as 500 mg per tablet. How many tablets should be taken?

**Answer a**

Start with 20 mg of Valium. For the conversion factor, we know that 10 mg Valium = 1 tablet

$$20 \cancel{\text{mg}} \times \frac{1 \text{ tablet}}{10 \cancel{\text{mg}}} = 2 \text{ tablets}$$

**Answer b**

Start with 1 g (1000 mg) of Calcium. For the conversion factor, we know that 500 mg Calcium = 1 tablet

$$1000 \cancel{\text{mg}} \times \frac{1 \text{ tablet}}{500 \cancel{\text{mg}}} = 2 \text{ tablets}$$

Drug Dosage Calculation based on Body Weight. Many drugs (especially in children) are dosed according to body weight (mg/kg). These calculations are carried in 3-step conversions. The first step is to convert the body weight from *pounds (lbs)* to *kg*. The second step is to convert *kg* to *mg* (the total *mg dose* calculated based on body weight). And, finally, the *mg dose* is converted to the number of *tablets*. (as in Example 1.8.1).

## ✓ Example 1.9.2

a. Demerol is ordered 1.5mg/kg for a patient that is 220 lbs. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?
b. A doctor prescribes amoxicillin 30mg/kg to a child weighing 73.5 lbs. Amoxicillin is available as 500 mg tablets. How many tablets should the nurse administer?

### Solution

a. We start with the given, 220 *lbs*. We want to change the unit from *lbs* to *kg*, and then, from *kg* to *total dose (mg)* and then *the mg dose to tablets*. The first conversion factor will cancel out the original unit, *lbs*, and introduce the unit we are converting to, which is *kg*. The second conversion factor will cancel out *kg*, and introduce the unit of the *dose* (usually *mg*) and then *mg* to *tablet*.

$$220 \cancel{\text{lbs}} \times \frac{1 \cancel{\text{kg}}}{2.2 \cancel{\text{lbs}}} \times \frac{1.5 \cancel{\text{mg}}}{1 \cancel{\text{kg}}} \times \frac{1 \text{ tablet}}{50 \cancel{\text{mg}}} = 3 \text{ tablets}$$

Hence, the nurse administers 3 tablets.

b. Start with the given, 73.5 *lbs*. We want to change the unit from *lbs* to *kg*, and then, from *kg* to total dose (*mg*) and then *mg* to *tablets*. The first conversion factor will cancel out the original unit, *lbs*, and convert to *kg*. The second conversion factor will cancel out *kg*, and convert to the total *mg dose* and the final conversion will cancel *mg* to introduce the final unit, *tablet*.

$$73.5 \cancel{\text{ lbs}} \times \frac{1 \cancel{\text{ kg}}}{2.2 \cancel{\text{ lbs}}} \times \frac{30 \cancel{\text{ mg}}}{1 \cancel{\text{ kg}}} \times \frac{1 \text{ tablet}}{500 \cancel{\text{ mg}}} = 2 \text{ tablets}$$

Hence, the nurse administers 2 tablets.

## ? Exercise 1.9.2

Calculate each of the following.

a. Vancomycin is ordered 15mg/kg for a patient that is 110 lbs. Vancomycin is available as 250 mg per capsule. How many capsules should the nurse administer? (ans. 3 capsules)
b. A doctor prescribes ampicillin 40mg/kg to a patient weighing 55 lbs. Ampicillin is available as 500 mg tablets. How many tablets should the nurse administer? (ans. 2 tablets)

**Answer a**

$$110 \cancel{\text{ lbs}} \times \frac{1 \cancel{\text{ kg}}}{2.2 \cancel{\text{ lbs}}} \times \frac{15 \cancel{\text{ mg}}}{1 \cancel{\text{ kg}}} \times \frac{1 \text{ tablet}}{250 \cancel{\text{ mg}}} = 3 \text{ tablets}$$

**Answer b**

$$55 \cancel{\text{ lbs}} \times \frac{1 \cancel{\text{ kg}}}{2.2 \cancel{\text{ lbs}}} \times \frac{40 \cancel{\text{ mg}}}{1 \cancel{\text{ kg}}} \times \frac{1 \text{ tablet}}{500 \cancel{\text{ mg}}} = 2 \text{ tablets}$$

## References


1. The Use of Body Surface Area as a Criterion of Drug Dosage in Cancer Chemotherapy(opens in new window) [cancerres.aacrjournals.org] "The Use of Body Surface Area as a Criterion of Drug Dosage in Cancer Chemotherapy" D Pinkel. Cancer Research 1958


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# 1.S: Chemistry, Matter, and Measurement (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

**Chemistry** is the study of **matter**, which is anything that has mass and takes up space. Chemistry is one branch of **science**, which is the study of the natural universe. Like all branches of science, chemistry relies on the **scientific method**, which is a process of learning about the world around us. In the scientific method, a guess or **hypothesis** is tested through experiment and measurement.

Matter can be described in a number of ways. **Physical properties** describe characteristics of a sample that do not change the chemical identity of the material (size, shape, color, and so on), while **chemical properties** describe how a sample of matter changes its chemical composition. A **substance** is any material that has the same physical and chemical properties throughout. An **element** is a substance that cannot be broken down into chemically simpler components. The smallest chemically identifiable piece of an element is an **atom**. A substance that can be broken down into simpler chemical components is a **compound**. The smallest chemically identifiable piece of a compound is a **molecule**. Two or more substances combine physically to make a **mixture**. If the mixture is composed of discrete regions that maintain their own identity, the mixture is a **heterogeneous mixture**. If the mixture is so thoroughly mixed that the different components are evenly distributed throughout, it is a **homogeneous mixture**. Another name for a homogeneous mixture is a **solution**. Substances can also be described by their **phase**: solid, liquid, or gas.

Scientists learn about the universe by making measurements of **quantities**, which consist of **numbers** (how many) and **units** (of what). The numerical portion of a quantity can be expressed using **scientific notation**, which is based on **powers**, or exponents, of 10. Large numbers have positive powers of 10, while numbers less than 1 have negative powers of 10. The proper reporting of a measurement requires proper use of **significant figures**, which are all the known digits of a measurement plus the first estimated digit. The number of figures to report in the result of a calculation based on measured quantities depends on the numbers of significant figures in those quantities. For addition and subtraction, the number of significant figures is determined by position; for multiplication and division, it is decided by the number of significant figures in the original measured values. Nonsignificant digits are dropped from a final answer in accordance with the rules of **rounding**.

Chemistry uses SI, a system of units based on seven **basic units**. The most important ones for chemistry are the units for length, mass, amount, time, and temperature. Basic units can be combined with numerical prefixes to change the size of the units. They can also be combined with other units to make **derived units**, which are used to express other quantities such as **volume**, **density**, or **energy**. A formal conversion from one unit to another uses a **conversion factor**, which is constructed from the relationship between the two units. Numbers in conversion factors may affect the number of significant figures in a calculated quantity, depending on whether the conversion factor is **exact**. Conversion factors can be applied in separate computations, or several can be used at once in a single, longer computation. Conversion factors are very useful in calculating **dosages**.

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# CHAPTER OVERVIEW

## 2: Energy and Chemical Processes

Energy is a vital component of the world around us. Nearly every physical and chemical process, including all the chemical reactions discussed in previous chapters, occurs with a simultaneous energy change. In this chapter, we will explore the nature of energy and how energy and chemistry are related.


2.1: Prelude to Energy and Chemical Processes
2.2: Energy and Its Units
2.3: Heat and Temperature
2.4: Phase Changes
2.5: The Energy of Biochemical Reactions
2.S: Energy and Chemical Processes (Summary)


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# 2.1: Prelude to Energy and Chemical Processes

*Metabolism* is the collective term for the chemical reactions that occur in cells and provide energy to keep cells alive. Some of the energy from metabolism is in the form of heat, and some animals use this heat to regulate their body temperatures. Such *warm-blooded* animals are called *endotherms*. In endotherms, problems with metabolism can lead to fluctuations in body temperature. When humans get sick, for instance, our body temperatures can rise higher than normal; we develop a fever. When food is scarce (especially in winter), some endotherms go into a state of controlled decreased metabolism called *hibernation*. During hibernation, the body temperatures of these endotherms actually decrease. In hot weather or when feverish, endotherms will pant or sweat to rid their bodies of excess heat.

Table **2.1.1**: Average Body Temperatures of Selected Endotherms

| Endotherm | Body Temperature (°F) | Body Temperature (°C) |
|---|---|---|
| bird | up to 110 | up to 43.5 |
| cat | 101.5 | 38.6 |
| dog | 102 | 38.9 |
| horse | 100.0 | 37.8 |
| human | 98.6 | 37.0 |
| pig | 102.5 | 39.2 |

*Ectotherms*, sometimes called *cold-blooded* animals, do not use the energy of metabolism to regulate body temperature. Instead, they depend on external energy sources, such as sunlight. Fish, for example, will seek out water of different temperatures to regulate body temperature. The amount of energy available is directly related to the metabolic rate of the animal. When energy is scarce, ectotherms may also hibernate.

The connection between metabolism and body temperature is a reminder that energy and chemical reactions are intimately related. A basic understanding of this relationship is especially important when those chemical reactions occur within our own bodies.

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# 2.2: Energy and Its Units

**Learning Objectives**

- To define *energy* and *heat.*
- To relate calories to nutrition and exercise.

Energy is the ability to do work. You can understand what this means by thinking about yourself when you feel “energetic.” You feel ready to go—to jump up and get something done. When you have a lot of energy, you can perform a lot of work. By contrast, if you do not feel energetic, you have very little desire to do much of anything. This description is not only applicable to you but also to all physical and chemical processes. The quantity of work that can be done is related to the quantity of energy available to do it.

Energy can be transferred from one object to another if the objects have different temperatures. The transfer of energy due to temperature differences is called heat. For example, if you hold an ice cube in your hand, the ice cube slowly melts as energy in the form of heat is transferred from your hand to the ice. As your hand loses energy, it starts to feel cold.

Because of their interrelationships, energy, work, and heat have the same units. The SI unit of energy, work, and heat is the joule (J). A joule is a tiny amount of energy. For example, it takes about 4 J to warm 1 mL of $H_2O$ by 1°C. Many processes occur with energy changes in thousands of joules, so the kilojoule (kJ) is also common. Another unit of energy, used widely in the health professions and everyday life, is the calorie (cal). The calorie was initially defined as the amount of energy needed to warm 1 g of $H_2O$ by 1°C, but in modern times, the calorie is related directly to the joule, as follows:

$$1\ cal = 4.184\ J \tag{2.2.1}$$

We can use this relationship to convert quantities of energy, work, or heat from one unit to another.

> *Although the joule is the proper SI unit for energy, we will use the calorie or the kilocalorie (or Calorie) in this chapter because they are widely used by health professional*

**Example 2.2.1**

The energy content of a single serving of bread is 70.0 Cal. What is the energy content in calories? In joules?

**Solution**

This is a simple conversion-factor problem. Using the relationship 1 Cal = 1,000 cal, we can answer the first question with a one-step conversion:

$$70.0\ \text{Cal} \times \frac{1,000\ \text{cal}}{1\ \text{Cal}} = 70,000\ \text{cal}$$

Then we convert calories into joules

$$70,000\ \text{cal} \times \frac{4.184\ \text{J}}{1\ \text{cal}} = 293,000\ \text{J}$$

and then kilojoules

$$293,000\ \text{J} \times \frac{1\ \text{kJ}}{1,000\ \text{J}} = 293\ \text{kJ}$$

The energy content of bread comes mostly from carbohydrates.

**Exercise 2.2.1**

The energy content of one cup of honey is 1,030 Cal. What is its energy content in calories and joules?

**Answer**

1,030,000 (1.03 x $10^6$) cal; 4,309,520 (4.31 x $10^6$) J

The calorie is used in nutrition to express the energy content of foods. However, because a calorie is a rather small quantity, nutritional energies are usually expressed in **kilocalories (kcal)**, also called **Calories (capitalized; Cal)**. For example, a candy bar may provide 120 Cal (nutritional calories) of energy, which is equal to 120,000 cal. Figure **2.2.1** shows an example.

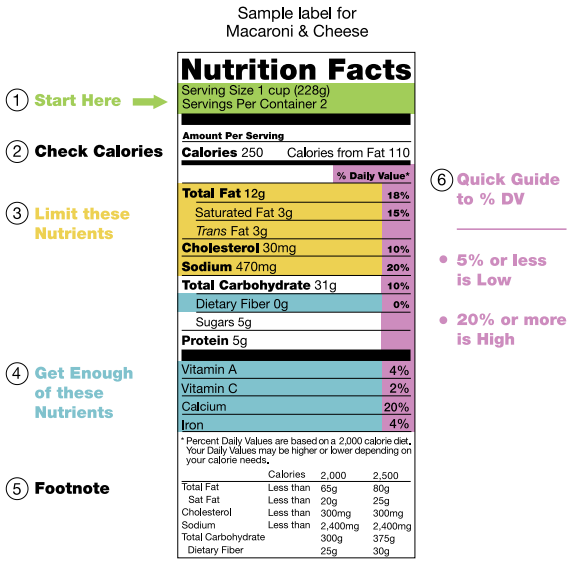



Figure **2.2.1**: Figure **2.2.1**: Nutritional Energy. A sample nutrition facts label, with instructions from the U.S. Food and Drug Administration. from Wikipedia.

The caloric content of foods is determined by analyzing the food for protein, carbohydrate, fat, water, and "minerals" and then calculating the caloric content using the average values for each component that produces energy (**9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals**). An example of this approach is shown in Table **2.2.1** for a slice of roast beef.

Table **2.2.1**: Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef

| Composition | Calories |
|---|---|
| 97.5 g of water | × 0 Cal/g = 0 |
| 58.7 g of protein | × 4 Cal/g = 235 |
| 69.3 g of fat | × 9 Cal/g = 624 |
| 0 g of carbohydrates | × 4 Cal/g = 0 |
| 1.5 g of minerals | × 0 Cal/g = 0 |
| **Total mass: 227.0 g** | **Total calories: about 900 Cal** |

The compositions and caloric contents of some common foods are given in **2.2.2**.

Table **2.2.2**: Approximate Compositions and Fuel Values of Some Common Foods

| Food (quantity) | Approximate Composition (%) | | | | Food Value (Cal/g) | Calories |
|---|---|---|---|---|---|---|
| | Water | Carbohydrate | Protein | Fat | | |
| beer (12 oz) | 92 | 3.6 | 0.3 | 0 | 0.4 | 150 |
| coffee (6 oz) | 100 | ~0 | ~0 | ~0 | ~0 | ~0 |
| milk (1 cup) | 88 | 4.5 | 3.3 | 3.3 | 0.6 | 150 |
| egg (1 large) | 75 | 2 | 12 | 12 | 1.6 | 80 |
| butter (1 tbsp) | 16 | ~0 | ~0 | 79 | 7.1 | 100 |
| apple (8 oz) | 84 | 15 | ~0 | 0.5 | 0.6 | 125 |
| bread, white (2 slices) | 37 | 48 | 8 | 4 | 2.6 | 130 |
| brownie (40 g) | 10 | 55 | 5 | 30 | 4.8 | 190 |
| hamburger (4 oz) | 54 | 0 | 24 | 21 | 2.9 | 326 |
| fried chicken (1 drumstick) | 53 | 8.3 | 22 | 15 | 2.7 | 195 |
| carrots (1 cup) | 87 | 10 | 1.3 | ~0 | 0.4 | 70 |

Because the Calorie represents such a large amount of energy, a few of them go a long way. An average 73 kg (160 lb) person needs about 67 Cal/h (1600 Cal/day) to fuel the basic biochemical processes that keep that person alive. This energy is required to maintain body temperature, keep the heart beating, power the muscles used for breathing, carry out chemical reactions in cells, and send the nerve impulses that control those automatic functions. Physical activity increases the amount of energy required but not by as much as many of us hope. A moderately active individual requires about 2500−3000 Cal/day; athletes or others engaged in strenuous activity can burn 4000 Cal/day. Any excess caloric intake is stored by the body for future use, usually in the form of fat, which is the most compact way to store energy. When more energy is needed than the diet supplies, stored fuels are mobilized and oxidized. We usually exhaust the supply of stored carbohydrates before turning to fats, which accounts in part for the popularity of low-carbohydrate diets.

## To Your Health: Energy Expenditures

Most health professionals agree that exercise is a valuable component of a healthy lifestyle. Exercise not only strengthens the body and develops muscle tone but also expends energy. After obtaining energy from the foods we eat, we need to expend that energy somehow, or our bodies will store it in unhealthy ways (e.g., fat). Like the energy content in food, the energy expenditures of exercise are also reported in kilocalories, usually kilocalories per hour of exercise. These expenditures vary widely, from about 440 kcal/h for walking at a speed of 4 mph to 1,870 kcal/h for mountain biking at 20 mph. Table **2.2.3** lists the energy expenditure for a variety of exercises.

Table **2.2.3**: Energy Expenditure of a 180-Pound Person during Selected Exercises

| Exercise | Energy Expended (kcal/h) |
|---|---|
| aerobics, low-level | 325 |
| basketball | 940 |
| bike riding, 20 mph | 830 |
| golfing, with cart | 220 |
| golfing, carrying clubs | 425 |
| jogging, 7.5 mph | 950 |
| racquetball | 740 |
| skiing, downhill | 520 |
| soccer | 680 |
| walking upstairs | 1,200 |
| yoga | 280 |

Because some forms of exercise use more energy than others, anyone considering a specific exercise regimen should consult with his or her physician first.

## Summary

Energy is the ability to do work. Heat is the transfer of energy due to temperature differences. Energy and heat are expressed in units of joules.

## Concept Review Exercises

1. What is the relationship between energy and heat?
2. What units are used to express energy and heat?

## Answers

1. Heat is the exchange of energy from one part of the universe to another. Heat and energy have the same units.
2. Joules and calories are the units of energy and heat.

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# 2.3: Heat and Temperature

**Learning Objectives**

- To relate heat transfer to temperature change.
- Memorize temperature equations for Celsius, Fahrenheit and Kelvin conversions.
- Understand how body temperature can vary.

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being "hot." Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as "cold." In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

## Temperature Scales

Temperature is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees. There are three scales used for reporting temperatures. Figure **2.3.1** compares the three temperature scales: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

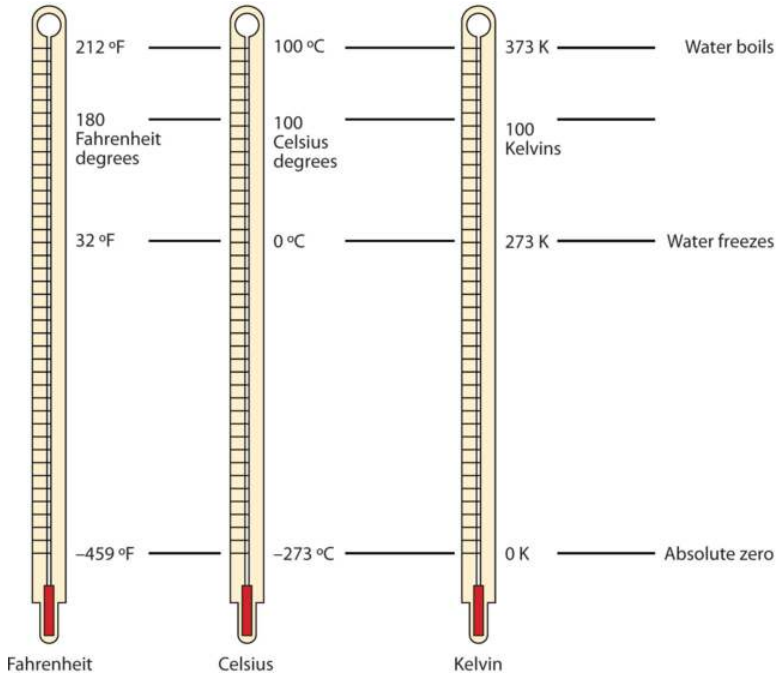



Figure **2.3.1**: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales. These thermometers have a red-colored liquid which contains alcohol and food coloring. Silver looking thermometers contain mercury, which is a neurotoxin.

In the United States, the commonly used temperature scale is the *Fahrenheit scale* (symbolized by °F and spoken as "degrees Fahrenheit"). On this scale, the freezing point of liquid water (the temperature at which liquid water turns to solid ice) is 32 °F, and the boiling point of water (the temperature at which liquid water turns to steam) is 212 °F.

Science also uses other scales to express temperature. For example, the Celsius scale (symbolized by °C and spoken as "degrees Celsius") defines 0°C as the freezing point of water and 100 °C as the boiling point of water. This scale is divided into 100

divisions between these two landmarks and extended higher and lower as well. By comparing the Fahrenheit and Celsius scales, a conversion between the two scales can be determined:

$$^{\circ}C = (^{\circ}F - 32) \times \frac{5}{9} \tag{2.3.1}$$

$$^{\circ}F = \left(^{\circ}C \times \frac{9}{5}\right) + 32 \tag{2.3.2}$$

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

**Example 2.3.1: Conversions**

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

**Solution**

a. Using Equation 2.3.1, we have

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

b. Using Equation 2.3.2, we have

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

For more examples of how to perform these types of problems, click on this video to see your professor in action.

**Exercise 2.3.1**

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

**Answer a**

−17.8°C

**Answer b**

414°F

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

$$K =^{\circ} C + 273.15 \tag{2.3.3}$$

For most purposes, it is acceptable to use 273 instead of 273.15 in Equation 2.3.3.

Note that the Kelvin scale does not use the word *degrees*; a temperature of 295 K is spoken of as “two hundred ninety-five kelvin” and not “two hundred ninety-five degrees Kelvin.”

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

### Example 2.3.2: Room Temperature

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

**Solution**

First, we use Equation 2.3.1 to determine the temperature in degrees Celsius:

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

Then we use Equation 2.3.3 to determine the temperature in the Kelvin scale:

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

So, room temperature is about 295 K.

### Health Application: Body temperature

Normal body temperature is defined as being 98.6°F (+/- 1.0°F). To determine body temperature, thermometers can be placed inside or on the surface of the body. The two best methods of obtaining body temperature are placing the thermometer either under the tongue or inside the rectum. Typically, children are capable of holding a thermometer in their mouths around the age of four (have fun before that age).

Fever is defined as body temperature being above 100°F (adults). High fever status occurs at and above 104°F. For adults, these adults should seek medical attention immediately if the fever exceeds 104°F. For children, these values are much lower.

Hyperthermia (inability of the body to regulate heat) occurs when normal body temperature is exceeded. Conditions that can cause hyperthermia are fever (infection), heat stroke, thyroid disorders, heart attack, or traumatic injury. Medications for cancer, arthritis, and thyroid patients can cause the body temperature to rise. Symptoms of hyperthermia include sweating, confusion, nausea, and dizziness.

Hypothermia (exposure to cold environments) occurs when normal body temperature dips below 95.0°F. When this occurs, the affected person(s) should seek immediate medical attention. During hypothermia, the body has problems producing heat. Medical conditions like diabetes, infection, and thyroid dysfunction can cause hypothermia. Watch this video of American Marines attempting to survive extreme environments. Symptoms of this condition involve shivering, confusion, and sluggish behavior.

Treating hyperthermia could involve hydrating a patient. If a fever is due to infection, analgesics (like Tylenol, Advil, aspirin, or Aleve) can help alleviate fever. Placing someone in a cool bath can also relieve symptoms.

To combat hypothermia, one must remove wet clothing, redress in warm materials, and participate in physical movement.

## Heat transfer

Heat is a familiar manifestation of energy. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from

our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

Suppose we consider the transfer of heat from the opposite perspective—namely, what happens to a system that gains or loses heat? Generally, the system’s temperature changes. (We will address a few exceptions later.) The greater the original temperature difference, the greater the transfer of heat, and the greater the ultimate temperature change.

## Summary

- Heat transfer is related to temperature change.

## Concept Review Exercise

1. Describe what happens when two objects that have different temperatures come into contact with one another.

## Answer

1. The temperature of the hot object decreases and the temperature of the cold object increases as heat is transferred from the hot object to the cold object. The change in temperature of each depends on the identity and properties of each substance.

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# 2.4: Phase Changes

**Learning Objectives**

- Determine the heat associated with a phase change.

Matter can exist in one of several different states, including a gas, liquid, or solid state. The amount of energy in molecules of matter determines the **state of matter**.

- A **gas** is a state of matter in which atoms or molecules have enough energy to move freely. The molecules come into contact with one another only when they randomly collide.
- A **liquid** is a state of matter in which atoms or molecules are constantly in contact but have enough energy to keep changing positions relative to one another.
- A **solid** is a state of matter in which atoms or molecules do not have enough energy to move. They are constantly in contact and in fixed positions relative to one another.

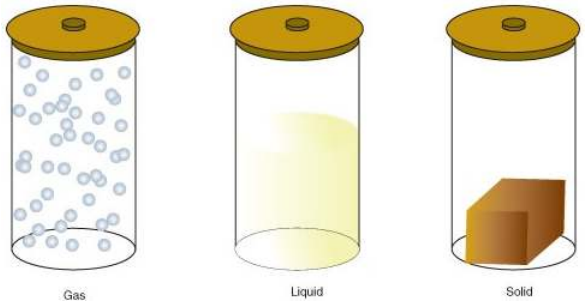



Figure **2.4.1**: States of Matter. All three containers contain a substance with the same mass, but the substances are in different states. In the left-hand container, the substance is a gas, which has spread to fill its container. It takes both the shape and volume of the container. In the middle container, the substance is a liquid, which has spread to take the shape of its container but not the volume. In the right-hand container, the substance is a solid, which takes neither the shape nor the volume of its container.

The following are the changes of state:

| | |
|---|---|
| Solid → Liquid | Melting or fusion |
| Liquid → Gas | Vaporization |
| Liquid → Solid | Freezing |
| Gas → Liquid | Condensation |
| Solid → Gas | Sublimation |

- If heat is added to a substance, such as in melting, vaporization, and sublimation, the process is **endothermic**. In this instance, heat is increasing the speed of the molecules causing them move faster (examples: solid to liquid; liquid to gas; solid to gas).
- If heat is removed from a substance, such as in freezing and condensation, then the process is **exothermic**. In this instance, heat is decreasing the speed of the molecules causing them move slower (examples: liquid to solid; gas to liquid). These changes **release heat** to the surroundings.
- The amount of heat needed to change a sample from solid to liquid would be the same to reverse from liquid to solid. The only difference is the direction of heat transfer.

**Example 2.4.1**

Label each of the following processes as endothermic or exothermic.

a. water boiling
b. ice forming on a pond

**Solution**

a. endothermic - you must put a pan of water on the stove and give it heat in order to get water to boil. Because you are adding heat/energy, the reaction is endothermic.
b. exothermic - think of ice forming in your freezer instead. You put water into the freezer, which takes heat out of the water, to get it to freeze. Because heat is being pulled out of the water, it is exothermic. Heat is leaving.

**Exercise 2.4.1**

Label each of the following processes as endothermic or exothermic.

a. water vapor condensing
b. gold melting

**Answer**

a. exothermic

b. endothermic

A phase change is a physical process in which a substance goes from one phase to another. Usually the change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The melting point is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The boiling point is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid or a liquid to a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water ($H_2O$) as an example. On the Celsius scale, $H_2O$ has a melting point of 0°C and a boiling point of 100°C. At 0°C, both the solid and liquid phases of $H_2O$ can coexist. However, if heat is added, some of the solid $H_2O$ will melt and turn into liquid $H_2O$. If heat is removed, the opposite happens: some of the liquid $H_2O$ turns into solid $H_2O$. A similar process can occur at 100°C: adding heat increases the amount of gaseous $H_2O$, while removing heat increases the amount of liquid $H_2O$ (Figure **2.4.1**).

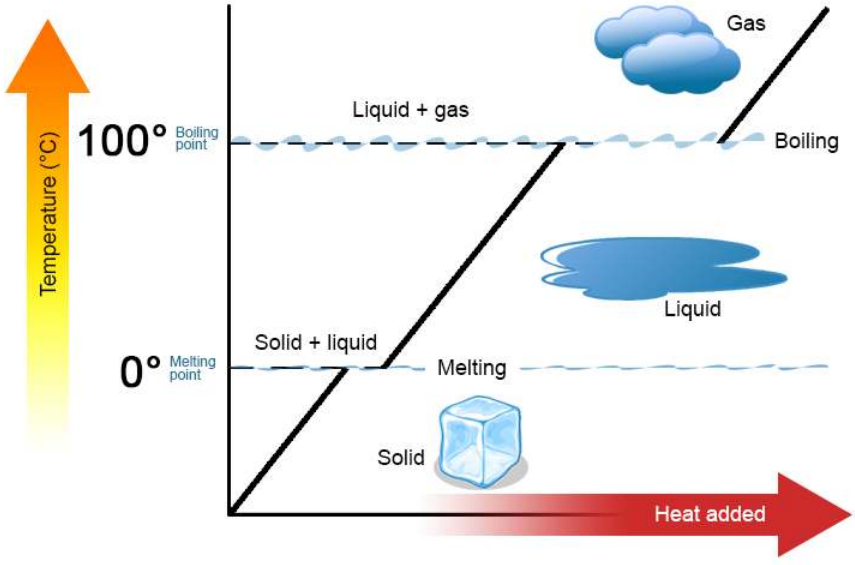



Figure **2.4.2**: Heating curve for water. As heat is added to solid water, the temperature increases until it reaches 0 °C, *the melting point. At this point, the phase change, added heat goes into changing the state from a solid to liquid. Only when this phase change is complete, the temperature can increase. (CC BY 3.0 Unported; Community College Consortium for Bioscience Credentials).*

Water is a good substance to use as an example because many people are already familiar with it. Other substances have melting points and boiling points as well.

Second, as shown in Figure **2.4.1**, **the temperature of a substance does not change** as the substance goes **from one phase to another**. In other words, phase changes are isothermal (isothermal means "constant temperature"). Again, consider $H_2O$ as an example. Solid water (ice) can exist at 0°C. If heat is added to ice at 0°C, some of the solid changes phase to make liquid, which is also at 0°C. Remember, the solid and liquid phases of $H_2O$ can coexist at 0°C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

1. What is the direction of heat transfer in boiling water?
2. What is the direction of heat transfer in freezing water?
3. What is the direction of heat transfer in sweating?

### Answers

1. Boiling. Heat is being added to the water to get it from the liquid state to the gas state.

2. Freezing. Heat is exiting the system in order to go from liquid to solid. Another way to look at it is to consider the opposite process of melting. Energy is consumed (endothermic) to melt ice (solid to liquid) so the opposite process (liquid to solid) must be exothermic.

3. Sweating. Heat is consumed to evaporate the moisture on your skin which lowers your temperature.

### Key Takeaway

- There is an energy change associated with any phase change.

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# 2.5: The Energy of Biochemical Reactions

**Learning Objectives**

- To relate the concept of energy change to chemical reactions that occur in the body.

The chemistry of the human body, or any living organism, is very complex. Even so, the chemical reactions found in the human body follow the same principles of energy that other chemical reactions follow.

Where does the energy that powers our bodies come from? The details are complex, but we can look at some simple processes at the heart of cellular activity.

An important reaction that provides energy for our bodies is the oxidation of glucose ($C_6H_{12}O_6$):

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(\ell)} + 670 \text{ kcal} \tag{2.5.1}$$

Considering that 1 mol of $C_6H_{12}O_6(s)$ has a volume of about 115 mL, we can see that glucose is a compact source of energy.

Glucose and other sugars are examples of carbohydrates, which are one of the three main dietary components of a human diet. All carbohydrates supply approximately 4 kcal/g. You can verify that by taking the heat of reaction for glucose oxidation and dividing it by its molar mass. Proteins, the building blocks of structural tissues like muscle and skin, also supply about 4 kcal/g. Other important energy sources for the body are fats, which are largely hydrocarbon chains. Fats provide even more energy per gram, about 9 kcal/g.

Another important reaction is the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP), which is shown in Figure **2.5.1**. Under physiological conditions, the breaking of an O–P bond and the formation of an O–P and two O–H bonds gives off about 7.5 kcal/mol of ATP. This may not seem like much energy, especially compared to the amount of energy given off when glucose reacts. It is enough energy, however, to fuel other biochemically important chemical reactions in our cells.

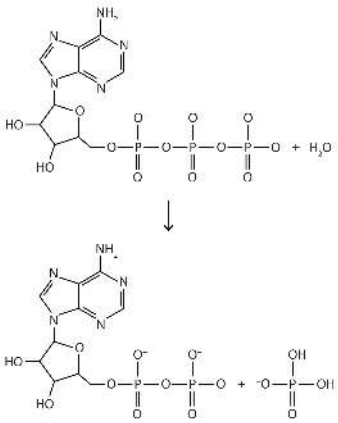


Figure **2.5.1**: ATP to ADP. The conversion of ATP (top) to ADP (bottom) provides energy for the cells of the body.

Even complex biological reactions must obey the basic rules of chemistry.

## Career Focus: Dietitian

A dietitian is a nutrition expert who communicates food-related information to the general public. In doing so, dietitians promote the general well-being among the population and help individuals recover from nutritionally related illnesses.

Our diet does not just supply us with energy. We also get vitamins, minerals, and even water from what we eat. Eating too much, too little, or not enough of the right foods can lead to a variety of problems. Dietitians are trained to make specific dietary recommendations to address particular issues relating to health. For example, a dietitian might work with a person to develop an overall diet that would help that person lose weight or control diabetes. Hospitals employ dietitians in planning menus for patients, and many dietitians work with community organizations to improve the eating habits of large groups of people.

## Concept Review Exercise

1. What is the energy content per gram of proteins, carbohydrates, and fats?

## Answer

1. proteins and carbohydrates: 4 kcal/g; fats: 9 kcal/g

## Key Takeaway

- Energy to power the human body comes from chemical reactions.

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# 2.S: Energy and Chemical Processes (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

**Energy** is the ability to do work. The transfer of energy from one place to another is **heat**. Heat and energy are measured in units of **joules**, **calories**, or kilocalories (equal to 1,000 calories).

Reactions that give off energy are called **exothermic**, while reactions that absorb energy are called **endothermic**. Energy-level diagrams can be used to illustrate the energy changes that accompany chemical reactions.

Even complex biochemical reactions have to follow the rules of simple chemistry, including rules involving energy change. Reactions of **carbohydrates** and **proteins** provide our bodies with about 4 kcal of energy per gram, while **fats** provide about 9 kcal per gram.

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# CHAPTER OVERVIEW

## 3: Elements, Atoms, and the Periodic Table

Just as a language has an alphabet from which words are built, chemistry has an alphabet from which matter is described. However, the chemical alphabet is larger than the one we use for spelling. You may have already figured out that the chemical alphabet consists of the chemical elements. Their role is central to chemistry, for they combine to form the millions and millions of known compounds.


3.1: Prelude to Elements, Atoms, and the Periodic Table
3.2: The Elements
3.3: Atomic Theory
3.4: The Structure of Atoms
3.5: Nuclei of Atoms
3.6: Atomic Masses
3.7: Arrangements of Electrons
3.8: The Periodic Table
3.S: Elements, Atoms, and the Periodic Table (Summary)


Template:HideTOC

*Thumbnail: Ionization energies superimposed on a periodic table. (CC BY-NC-SA; anonymous by request).*


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# 3.1: Prelude to Elements, Atoms, and the Periodic Table

The hardest material in the human body is tooth enamel. It has to be hard so that our teeth can serve us for a lifetime of biting and chewing; however, tough as it is, tooth enamel is susceptible to chemical attack. Acids found in some foods or made by bacteria that feed on food residues on our teeth are capable of dissolving enamel. Unprotected by enamel, a tooth will start to decay, thus developing cavities and other dental problems.

In the early 1900s, a dentist in Colorado Springs, Colorado, noted that many people who lived in the area had brown-stained teeth that, while unsightly, were surprisingly resistant to decay. After years of study, excess fluorine compounds in the drinking water were discovered to be the cause of both these effects. Research continued, and in the 1930s, the US Public Health Service found that low levels of fluorine in water would provide the benefit of resisting decay without discoloring teeth.

The protective effects of fluorine have a simple chemical explanation. Tooth enamel consists mostly of a mineral called hydroxyapatite, which is composed of calcium, phosphorus, oxygen, and hydrogen. We know now that fluorine combines with hydroxyapatite to make fluorapatite, which is more resistant to acidic decay than hydroxyapatite is. Currently about 50% of the US population drinks water that has some fluorine added (in the form of sodium fluoride, NaF) to reduce tooth decay. This intentional fluoridation, coupled with the use of fluoride-containing toothpastes and improved oral hygiene, has reduced tooth decay by as much as 60% in children. The nationwide reduction of tooth decay has been cited as an important public health advance in history. (Another important advance was the eradication of polio.)

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# 3.2: The Elements

**Learning Objectives**

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

An element is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure **3.2.1** shows some of the chemical elements.



Figure **3.2.1**: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

## Abundance

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

Table **3.2.1**: Elemental Composition of Earth

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

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

On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen, the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table **3.2.1** lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table **3.2.2** lists the relative abundances of elements in the human body. If you compare Table **3.2.1** and Table **3.2.2**, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table **3.2.1**; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table **3.2.2**: Elemental Composition of a Human Body

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

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

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

### LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

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

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

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

## Names and Symbols

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

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

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table **3.2.3** lists the names and symbols of some of the most familiar elements.

Table **3.2.3**: Element Names and Symbols

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

*The symbol comes from the Latin name of element.

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

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

### Example 3.2.1

Write the chemical symbol for each element without consulting Table **3.2.3** "Element Names and Symbols".

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

**Answer a**

Br

**Answer b**

B

**Answer c**

C

**Answer d**

Ca

**Answer e**

Au

## Exercise 3.2.1

Write the chemical symbol for each element without consulting Table 3.2.3.

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

**Answer a**

Mn

**Answer b**

Mg

**Answer c**

Ne

**Answer d**

N

**Answer e**

Ag

## Example 3.2.2

What element is represented by each chemical symbol?

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

**Answer a**

sodium

**Answer b**

mercury

**Answer c**

phosphorus

**Answer d**

potassium

**Answer e**

iodine

**? Exercise 3.2.2**

What element is represented by each chemical symbol?

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

**Answer a**

lead

**Answer b**

tin

**Answer c**

uranium

**Answer d**

oxygen

**Answer e**

fluorine

## Concept Review Exercises

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

## Answers

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

## Key Takeaways

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

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# 3.3: Atomic Theory

**Learning Objectives**

- Explain how all matter is composed of atoms.
- Describe the modern atomic theory.
- Recognize which elements exist as diatomic molecules.

Take some aluminum foil. Cut it in half. Now you have two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil.

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

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure **3.3.1**), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only $5.4 \times 10^{-10}$ m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

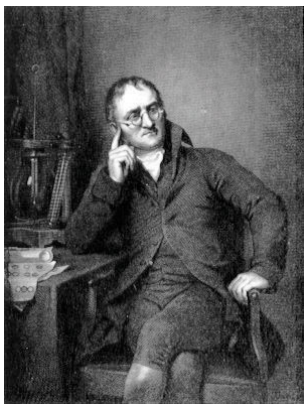


Figure **3.3.1** John Dalton was an English scientist who enunciated the modern atomic theory.

Most elements in their pure form exist as **individual atoms**. For example, a macroscopic chunk of iron (Fe) metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called **diatomic molecules**. In representing a diatomic molecule, we use the symbol of the element and include the ***subscript*** "2" to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen ($H_2$), nitrogen ($N_2$), fluorine ($F_2$), oxygen ($O_2$), iodine ($I_2$), chlorine ($Cl_2$) and bromine ($Br_2$). A few other elements can exist as 3-atom molecules like ozone ($O_3$) and 4-atom molecules like phosphorus ($P_4$). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is $S_8$ (Figure **3.3.2**).

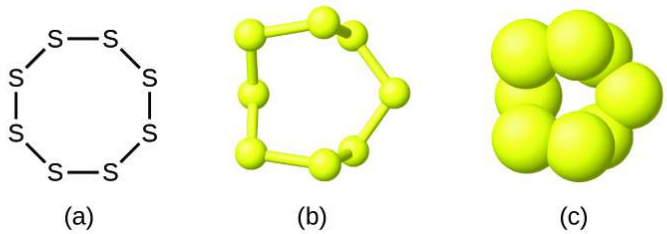



Figure **3.3.2**: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as $S_8$. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, $H_2$ and 2H represent distinctly different species. $H_2$ is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are **not** combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure **3.3.3**).

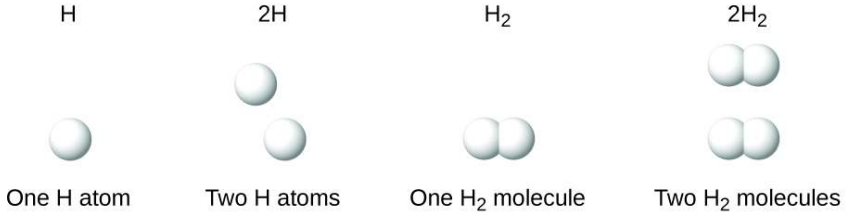



Figure **3.3.3**: The symbols H, 2H, $H_2$, and $2H_2$ represent very different entities.

## Example 3.3.1

Write the chemical formula of the following elements:

a. oxygen
b. carbon
c. potassium

**Solution**

Memorizing the diatomic molecules is worthwhile for our future endeavors. A mnemonic device to help in the memorization of the diatomic elements is as follows: **H**ave **N**o **F**ear **O**f **I**ce **C**old **B**eer. (hydrogen, nitrogen, fluorine, oxygen, iodine, chlorine and bromine).

a. Oxygen is one of the seven diatomic molecular elements. Its chemical formula is $O_2$.
b. Carbon is monatomic, hence its formula is C.
c. Potassium is monatomic hence its formula is K.

## Exercise 3.3.1

Write the chemical formula of the following elements:

a. hydrogen
b. nitrogen
c. neon

**Answer a**

Hydrogen is one of the seven diatomic molecular elements. Its chemical formula is $H_2$.

**Answer b**

Nitrogen is one of the seven diatomic molecular elements. Its chemical formula is $N_2$.

**Answer c**

Neon is a monatomic element, hence its formula is Ne.

## Looking Closer: Atomic Theory

Dalton's ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means "indivisible" or "uncuttable.") Dalton had something that the ancient Greek philosophers didn't have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was

> being used to study nature. So when Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

## Concept Review Exercises

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

## Answers

1. The modern atomic theory states that all matter is composed of atoms.
2. Atoms are the smallest parts of an element that maintain the identity of that element.

## Key Takeaways

- **Atoms** are the ultimate building blocks of all matter.
- The modern atomic theory establishes the concepts of **atoms** and how they compose matter.
- The **diatomic** elements are hydrogen, nitrogen, fluorine, oxygen, iodine, chlorine and bromine.

## Contributors and Attributions

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# 3.4: The Structure of Atoms

**Learning Objectives**

- Describe the three main subatomic particles.
- State how the subatomic particles are arranged in atoms.

There have been several minor but important modifications to Dalton's atomic theory. For one thing, Dalton considered atoms to be indivisible. We know now that atoms not only can be divided but also are composed of three different kinds of particle, *subatomic particles*, with their own properties that are different from the chemical properties of atoms.

## Subatomic Particles

The first subatomic particle was identified in 1897 and called the electron. It is an extremely tiny particle, with a mass of about $9.109 \times 10^{-31}$ kg. Experiments with magnetic fields showed that the electron has a negative electrical charge. By 1920, experimental evidence indicated the existence of a second particle. A proton has the same amount of charge as an electron, but its charge is positive, not negative. Another major difference between a proton and an electron is mass. Although still incredibly small, the mass of a proton is $1.673 \times 10^{-27}$ kg, which is almost 2,000 times greater than the mass of an electron. Because opposite charges attract each other (while like charges repel each other), protons attract electrons (and vice versa).

Finally, additional experiments pointed to the existence of a third particle. Evidence produced in 1932 established the existence of the neutron, a particle with about the same mass as a proton but with no electrical charge, it is *neutral*. We understand now that all atoms can be broken down into subatomic particles: protons, neutrons, and electrons. Table **3.4.1** lists some of their important characteristics and the symbols used to represent each particle.

Table **3.4.1**: Properties of the Subatomic Particles

| Particle | Symbol | Mass (kg) | Relative Mass (proton = 1) | Relative Charge |
|---|---|---|---|---|
| proton | $p^+$ | $1.673 \times 10^{-27}$ | 1 | +1 |
| neutron | $n^0$ | $1.675 \times 10^{-27}$ | 1 | 0 |
| electron | $e^-$ | $9.109 \times 10^{-31}$ | 0.00055 | −1 |

## The Nucleus

How are these subatomic particles arranged? Between 1909 and 1911, Ernest Rutherford, a Cambridge physicist, and his associates Hans Geiger and Ernest Marsden performed experiments that provided strong evidence concerning the internal structure of an atom. They took a very thin metal foil, such as gold or platinum, and aimed a beam of positively charged particles (called alpha particles, which are combinations of two protons and two neutrons) from a radioactive source toward the foil. Surrounding the foil was a detector—either a scintillator (a material that glows when hit by such particles) or some unexposed film (which is exposed where the particles hit it). The detector allowed the scientists to determine the distribution of the alpha particles after they interacted with the foil. Figure **3.4.1** shows a diagram of the experimental setup.

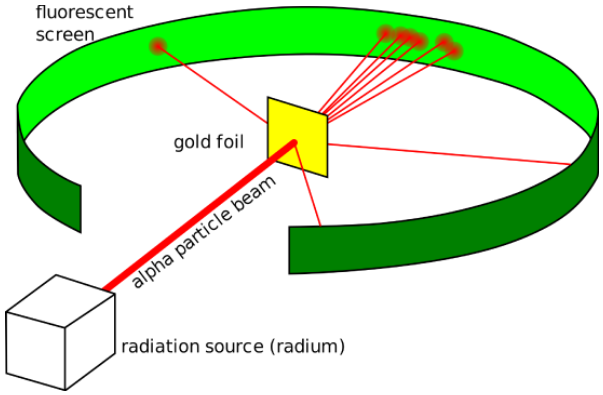



Figure **3.4.1**: The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. In this experiment, most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward the source. This was unexpected. Rutherford once said, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." (CC SA-BY 3.0; Kurzon).

Rutherford proposed the following model to explain these experimental results. Protons and neutrons are concentrated in a central region he called the nucleus (plural, *nuclei*) of the atom. Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom's size. As a result, an atom consists largely of empty space. Rutherford called his description the "planetary model" of the atom. Figure **3.4.2** shows how this model explains the experimental results.

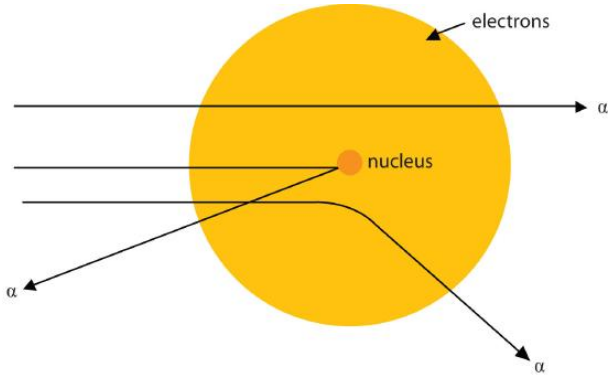



Figure **3.4.2**: Rutherford's Metal Foil Experiments. Rutherford explained the results of the metal foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles go straight through the empty space, a few particles are deflected, and fewer still ricochet back toward the source. The nucleus is much smaller proportionately than depicted here.

> *The planetary model of the atom replaced the plum pudding model, which had electrons floating around aimlessly like plums in a "pudding" of positive charge.*

Rutherford's model is essentially the same model that we use today to describe atoms but with one important modification. The planetary model suggests that electrons occupy certain specific, circular orbits about the nucleus. We know now that this model is overly simplistic. A better description is that electrons form fuzzy clouds around nuclei. Figure **3.4.3** shows a more modern version of our understanding of atomic structure.

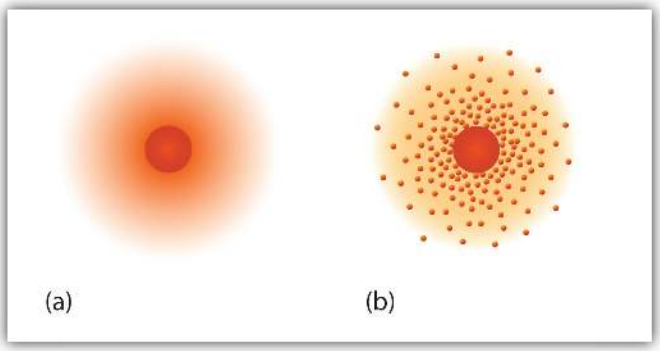



Figure **3.4.3**: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the color, the higher the probability that an electron will be at that point. (b) In a two-dimensional cross section of the electron in a hydrogen atom, the more crowded the dots, the higher the probability that an electron will be at that point. In both (a) and (b), the nucleus is in the center of the diagram.

## Concept Review Exercises

1. What are the charges and the relative masses of the three subatomic particles?
2. Describe the structure of an atom in terms of its protons, neutrons, and electrons.

## Answers

1. proton: +1, large; neutron: 0, large; electron: −1, small
2. Protons and neutrons are located in a central nucleus, while electrons orbit about the nucleus.

## Key Takeaways

- Atoms are composed of three main subatomic particles: protons, neutrons, and electrons.
- Protons and neutrons are grouped together in the nucleus of an atom, while electrons orbit about the nucleus.

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# 3.5: Nuclei of Atoms

**Learning Objectives**

- Define and differentiate between the atomic number and the mass number of an element.
- Explain how isotopes differ from one another.

Now that we know how atoms are generally constructed, what do atoms of any particular element look like? How many protons, neutrons, and electrons are in a specific kind of atom? First, if an atom is electrically neutral overall, then the number of protons equals the number of electrons. Because these particles have the same but opposite charges, equal numbers cancel out, producing a neutral atom.

## Atomic Number

In the 1910s, experiments with x-rays led to this useful conclusion: the magnitude of the positive charge in the nucleus of every atom of a particular element is the same. In other words, all atoms of the same element have the same number of protons. Furthermore, different elements have a different number of protons in their nuclei, so the number of protons in the nucleus of an atom is characteristic of a particular element. This discovery was so important to our understanding of atoms that the number of protons in the nucleus of an atom is called the atomic number (Z).

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Table **3.5.1** lists some common elements and their atomic numbers. Based on its **atomic number**, you can determine the **number of protons in the nucleus** of an atom. The largest atoms have over 100 protons in their nuclei.

**Example 3.5.1**

What is the number of protons in the nucleus of each element?

a. aluminum
b. iron
c. carbon

**Answer a**

According to Table 2.4.1, aluminum has an atomic number of 13. Therefore, every aluminum atom has 13 protons in its nucleus.

**Answer b**

Iron has an atomic number of 26. Therefore, every iron atom has 26 protons in its nucleus.

**Answer c**

Carbon has an atomic number of 6. Therefore, every carbon atom has 6 protons in its nucleus.

**Exercise 3.5.1**

What is the number of protons in the nucleus of each element? Use Table 2.4.1.

a. sodium
b. oxygen
c. chlorine

**Answer a**

Sodium has 11 protons in its nucleus.

**Answer b**

Oxygen has 8 protons in its nucleus.

**Answer c**

Chlorine has 17 protons in its nucleus

How many electrons are in an atom? Previously we said that for an electrically neutral atom, the **number of electrons equals the number of protons**, so the total opposite charges cancel. Thus, the **atomic number** of an element also gives the **number of electrons** in an atom of that element. (Later we will find that some elements may gain or lose electrons from their atoms, so those atoms will no longer be electrically neutral. Thus we will need a way to differentiate the number of electrons for those elements.)

### Example 3.5.2

How many electrons are present in the atoms of each element?

a. sulfur
b. tungsten
c. argon

**Answer a**

The atomic number of sulfur is 16. Therefore, in a neutral atom of sulfur, there are 16 electrons.

**Answer b**

The atomic number of tungsten is 74. Therefore, in a neutral atom of tungsten, there are 74 electrons.

**Answer c**

The atomic number of argon is 18. Therefore, in a neutral atom of argon, there are 18 electrons.

### Exercise 3.5.2

How many electrons are present in the atoms of each element?

a. magnesium
b. potassium
c. iodine

**Answer a**

Mg has 12 electrons.

**Answer b**

K has 19 electrons.

**Answer c**

I has 53 electrons.

Table **3.5.1**: Some Common Elements and Their Atomic Numbers

| Element | Atomic Number | Element | Atomic Nmbers |
|---|---|---|---|
| aluminum (Al) | 13 | magnesium (Mg) | 12 |
| americium (Am) | 95 | manganese (Mn) | 25 |
| argon (Ar) | 18 | mercury (Hg) | 80 |
| barium (Ba) | 56 | neon (Ne) | 10 |
| beryllium (Be) | 4 | nickel (Ni) | 28 |
| bromine (Br) | 35 | nitrogen (N) | 7 |
| calcium (Ca) | 20 | oxygen (O) | 8 |
| carbon (C) | 6 | phosphorus (P) | 15 |
| chlorine (Cl) | 17 | platinum (Pt) | 78 |
| chromium (Cr) | 24 | potassium (K) | 19 |
| cesium (Cs) | 55 | radon (Rn) | 86 |
| fluorine (F) | 9 | silver (Ag) | 47 |
| gallium (Ga) | 31 | sodium (Na) | 11 |
| gold (Au) | 79 | strontium (Sr) | 38 |
| helium (He) | 2 | sulfur (S) | 16 |
| hydrogen (H) | 1 | titanium (Ti) | 22 |
| iron (Fe) | 26 | tungsten (W) | 74 |
| iodine (I) | 53 | uranium (U) | 92 |
| lead (Pb) | 82 | zinc (Zn) | 30 |
| lithium (Li) | 3 | zirconium (Zr) | 40 |

## Isotopes

How many neutrons are in atoms of a particular element? At first it was thought that the number of neutrons in a nucleus was also characteristic of an element. However, it was found that atoms of the same element can have *different* numbers of neutrons. Atoms of the same element (i.e., same atomic number, Z) that have different numbers of neutrons are called isotopes. For example, 99% of the carbon atoms on Earth have 6 neutrons and 6 protons in their nuclei; about 1% of the carbon atoms have 7 neutrons in their nuclei. Naturally occurring carbon on Earth, therefore, is actually a mixture of isotopes, albeit a mixture that is 99% carbon with 6 neutrons in each nucleus.

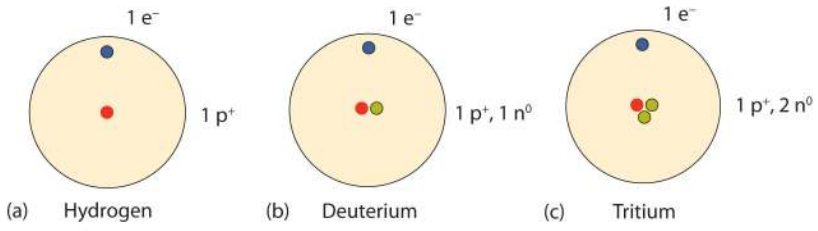



Figure **3.5.1**: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

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 **3.5.1** compares the three isotopes of hydrogen.

> 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.

Most elements exist as mixtures of isotopes. In fact, 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. The *mass number* (A) of an atom is the sum of the numbers of protons and neutrons in the nucleus. Given the mass number for a nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

A simple way of indicating the mass number of a particular isotope is to list it as a superscript on the left side of an element's symbol. Atomic numbers are often listed as a subscript on the left side of an element's symbol. Thus, we might see

$$\begin{matrix}\text{mass number}\longrightarrow 56\\ \text{atomic number}\longrightarrow 26\end{matrix}\mathrm{Fe} \tag{3.5.1}$$

which indicates a particular isotope of iron. The 26 is the atomic number (which is the same for all iron atoms), while the 56 is the mass number of the isotope. To determine the number of neutrons in this isotope, we subtract 26 from 56: 56 − 26 = 30, so there are 30 neutrons in this atom.

### ✔ Example 3.5.3

How many protons and neutrons are in each atom?

a. $^{35}_{17}\mathrm{Cl}$
b. $^{127}_{53}\mathrm{I}$

**Answer a**

In $^{35}_{17}\mathrm{Cl}$ there are 17 protons, and 35 − 17 = 18 neutrons in each nucleus.

**Answer b**

In $^{127}_{53}\mathrm{I}$ there are 53 protons, and 127 − 53 = 74 neutrons in each nucleus.

### ? Exercise 3.5.3

How many protons and neutrons are in each atom?

a. $^{197}_{79}\mathrm{Au}$
b. $^{23}_{11}\mathrm{Na}$

**Answer a**

In $^{197}_{79}\mathrm{Au}$ there are 79 protons, and 197 − 79 = 118 neutrons in each nucleus.

**Answer b**

In $^{23}_{11}\mathrm{Na}$ there are 11 protons, and 23 − 11 = 12 neutrons in each nucleus.

It is not absolutely necessary to indicate the atomic number as a subscript because each element has its own unique atomic number. Many isotopes are indicated with a superscript only, such as $^{13}\mathrm{C}$ or $^{235}\mathrm{U}$. You may also see isotopes represented in print as, for example, carbon-13 or uranium-235.

## Summary

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the **atomic number (Z)**. Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number (A)**, which is the **sum of the numbers of protons and neutrons**.

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure **3.5.2**.

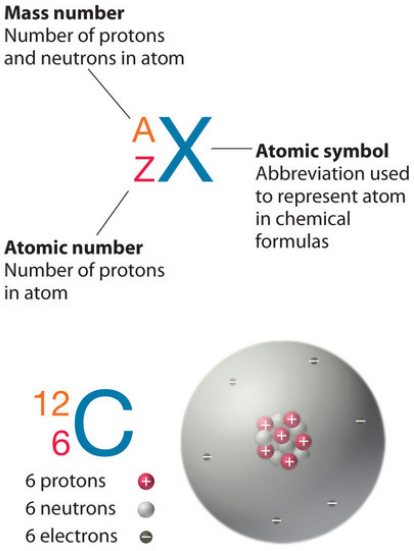



Figure **3.5.2**: Formalism used for identifying specific nuclide (any particular kind of nucleus)

The atomic symbol, X, is the abbreviation used to represent an atom in chemical formulas. The mass number, A, is the number of protons and neutrons in the atom, which is to the left of the X. The atomic number, Z, is the number of protons in the atom, which is to the left of the X and below the A.

## 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.

## Key Takeaways

- Each element is identified by its atomic number. The atomic number provides the element's location on the periodic table
- The isotopes of an element have different masses and are identified by their mass numbers.

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# 3.6: Atomic Masses

**Learning Objectives**

- Define atomic mass and atomic mass unit.
- Calculate atomic mass.

Even though atoms are very tiny pieces of matter, they have mass. Their masses are so small, however, that chemists often use a unit other than grams to express them—the atomic mass unit.

## Atomic Mass Unit

The atomic mass unit (abbreviated u, although amu is also used) is defined as 1/12 of the mass of a $^{12}C$ atom:

$$1\ \text{u} = \frac{1}{12}\ \text{the mass of}\ ^{12}\text{C atom} \tag{3.6.1}$$

It is equal to $1.661 \times 10^{-24}$ g.

Masses of other atoms are expressed with respect to the atomic mass unit. For example, the mass of an atom of $^{1}H$ is 1.008 u, the mass of an atom of $^{16}O$ is 15.995 u, and the mass of an atom of $^{32}S$ is 31.97 u. Note, however, that these masses are for particular isotopes of each element. Because most elements exist in nature as a mixture of isotopes, any sample of an element will actually be a mixture of atoms having slightly different masses (because neutrons have a significant effect on an atom's mass). How, then, do we describe the mass of a given element? By calculating an average of an element's atomic masses, weighted by the natural abundance of each isotope, we obtain a weighted average mass called the atomic mass (also commonly referred to as the *atomic weight*) of an element.

### Atomic Mass is the Weighted Average Mass of Isotopes

As stated above, most elements occur naturally as a mixture of two or more isotopes. Listed below (Table **3.6.1**) are the naturally occurring isotopes of selected elements along with the percent natural abundance of each.

Table **3.6.1**: Atomic Masses and Percent Abundances of Some Natural Isotopes

| Element | Isotope (Symbol) | Percent Natural Abundance | Atomic Mass (amu) | Average Atomic Mass (amu) |
|---|---|---|---|---|
| Hydrogen | $^{1}_{1}H$ | 99.985 | 1.0078 | 1.0079 |
| | $^{2}_{1}H$ | 0.015 | 2.0141 | |
| | $^{3}_{1}H$ | negligible | 3.0160 | |
| Carbon | $^{12}_{6}C$ | 98.89 | 12.000 | 12.011 |
| | $^{13}_{6}C$ | 1.11 | 13.003 | |
| | $^{14}_{6}C$ | trace | 14.003 | |
| Oxygen | $^{16}_{8}O$ | 99.759 | 15.995 | 15.999 |
| | $^{17}_{8}O$ | 0.037 | 16.995 | |
| | $^{18}_{8}O$ | 0.204 | 17.999 | |
| Chlorine | $^{35}_{17}Cl$ | 75.77 | 34.969 | 35.453 |
| | $^{38}_{17}Cl$ | 24.23 | 36.966 | |
| Copper | $^{63}_{29}Cu$ | 69.17 | 62.930 | 63.546 |
| | $^{65}_{29}Cu$ | 30.83 | 64.928 | |

For some elements, one particular isotope is much more abundant than any other isotopes. For example, naturally occurring hydrogen is nearly all hydrogen-1, and naturally occurring oxygen is nearly all oxygen-16. For many other elements, however, more than one isotope may exist in substantial quantities. Chlorine (atomic number 17) is yellowish-green toxic gas. About three quarters of all chlorine atoms have 18 neutrons, giving those atoms a mass number of 35. About one quarter of all chlorine atoms have 20 neutrons, giving those atoms a mass number of 37. Were you to simply calculate the arithmetic average of the precise atomic masses, you would get approximately 36.

$$\frac{34.969\,u + 36.966\,u}{2} = 35.968\,u$$

As you can see, the average atomic mass given in the last column of the table above (35.453) is significantly lower. Why? The reason is that we need to take into account the natural abundance percentages of each isotope in order to calculate what is called the **weighted average**. The atomic mass *of an element is the weighted average of the atomic masses of the naturally occurring isotopes of that element.*

$$0.7577\,(34.969\,u) + 0.2423\,(36.966\,u) = 35.453\,u$$

The weighted average is determined by multiplying the percent of natural abundance by the actual mass of the isotope. This is repeated until there is a term for each isotope. For chlorine, there are only two naturally occurring isotopes so there are only two terms.

Atomic mass = (%1)(mass 1) + (%2)(mass 2) + ⋯

Another example: oxygen exists as a mixture that is 99.759% $^{16}O$, 0.037% $^{17}O$ and 0.204% $^{18}O$. The atomic mass of oxygen (use percent natural abundance data from Table 2.5.1) would be calculated as follows:

Atomic mass = (%1)(mass 1) + (%2)(mass 2) + (%3)(mass 3)

$$0.99759\,(15.995u) + 0.00037\,(16.995u) + 0.00204\,(17.999u) = 15.999u$$

To confirm your answer, compare the calculated value to the weighted mass displayed on the periodic table.

### Example 3.6.1

Calculate the atomic mass of oxygen. Oxygen exists as a mixture of 3 isotopes. Their respective masses and natural abundance are shown below.

- $^{16}$O: 15.995 u (99.759%)
- $^{17}$O: 16.995 u (0.037%)
- $^{18}$O: 17.999 u (0.204%)

**Solution**

Multiply the isotope abundance by the actual mass of the isotope, and then sum up the products.

$$0.99759\,(15.995\,u) + 0.00037\,(16.995\,u) + 0.00204\,(17.999\,u) = 15.999\,u$$

### 3.6.1 Exercise

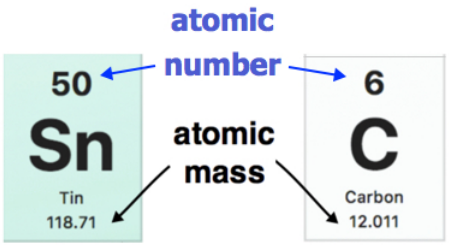
Calculate the atomic mass of copper. Copper exists as a mixture of 2 isotopes. Their respective masses and natural abundance are shown below.

- $^{63}$Cu: 62.930 u (69.17%)
- $^{65}$Cu: 64.928 u (30.83%)

**Answer**

63.546 u

The **atomic mass** of each element is found under the element symbol in the **periodic table.** Examples are shown below. The atomic mass of tin (Sn) is 118.71 u while the atomic mass of carbon (C) is 12.011 u. On the other hand, the **atomic number (Z)** of each element is found **above** the atomic symbol.




Atomic mass indicated on entries of the Periodic Table. (public Domain; Pubchem)

The **periodic table** is found in this link:

https://pubchem.ncbi.nlm.nih.gov/periodic-table/png/Periodic_Table_of_Elements_w_Atomic_Mass_PubChem.png

### Example 3.6.2: Mass of Carbon

What is the average mass of a carbon atom in grams? The atomic mass is found in the Periodic Table. Please use two decimal places.

**Solution**

This is a simple one-step conversion, similar to conversions we did in Chapter 1. We use the fact that 1 u = $1.661 \times 10^{-24}$ g:

$$12.01\ \cancel{u} \times \frac{1.661 \times 10^{-24}\ \text{g}}{1\ \cancel{u}} = 1.995 \times 10^{-23}\ \text{g}$$

This is an extremely small mass, which illustrates just how small individual atoms are.

**? Exercise 3.6.2: Mass of Tin**

What is the average mass of a tin atom in grams? The average atomic mass is found in the Periodic Table. Please use two decimal places.

**Answer**

$$118.71 \cancel{u} \times \frac{1.661 \times 10^{-24}\ \text{g}}{1\ \cancel{u}} = 1.972 \times 10^{-22}\ \text{g}$$

## Concept Review Exercises

1. Define atomic mass. Why is it considered a weighted average?
2. What is an atomic mass unit?

## Answers

1. The atomic mass is an average of an element's atomic masses, weighted by the natural abundance of each isotope of that element. It is a weighted average because different isotopes have different masses.
2. An atomic mass unit is 1/12th of the mass of a $^{12}C$ atom.

## Key Takeaway

- Atoms have a mass that is based largely on the number of protons and neutrons in their nucleus.
- The atomic mass of each element in the Periodic Table is the weighted average of the mass of all its isotopes.

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# 3.7: Arrangements of Electrons

**Learning Objectives**

- Describe how electrons are grouped within atoms.

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

The modern theory of electron behavior is called quantum mechanics. It makes the following statements about electrons in atoms:

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

Table **3.7.1**: Shells and Subshells

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

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

Table **3.7.2**: Number of Electrons

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

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

We use numbers to indicate which shell an electron is in. As shown in Table **3.7.1**, the first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1*s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $\mathbf{1}s^{\mathbf{1}}$ to describe the electronic structure of hydrogen. This structure is called an electron configuration. Electron configurations are shorthand descriptions of the arrangements of electrons in atoms. The electron configuration of a hydrogen atom is spoken out loud as “one-ess-one.”

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

The 1*s* subshell cannot hold 3 electrons (because an *s* subshell can hold a maximum of 2 electrons), so the electron configuration for a lithium atom cannot be $1s^3$. Two of the lithium electrons can fit into the 1*s* subshell, but the third electron must go into the second shell. The second shell has two subshells, *s* and *p*, which fill with electrons in that order. The 2*s* subshell holds a maximum of 2 electrons, and the 2*p* subshell holds a maximum of 6 electrons. Because lithium’s final electron goes into the 2*s* subshell, we write the electron configuration of a lithium atom as $\mathbf{1}s^2\mathbf{2}s^1$**.** The shell diagram for a lithium atom is shown below. 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.

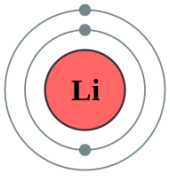



Figure **3.7.1**: Shell diagram of lithium (Li) atom.

The next largest atom, beryllium, has 4 electrons, so its electron configuration is $1s^22s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms start filling the 2*p* subshell. Thus, the electron configurations for the next six atoms are as follows:

- B: $1s^22s^22p^1$
- C: $1s^22s^22p^2$
- N: $1s^22s^22p^3$
- O: $1s^22s^22p^4$
- F: $1s^22s^22p^5$
- Ne: $1s^22s^22p^6$

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

Electron filling always starts with **1*s***, the subshell closest to the nucleus. Next is **2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5s, 4d, 5p, 6s,** etc., shown in the electron shell filling order diagram in Figure **3.7.2**. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

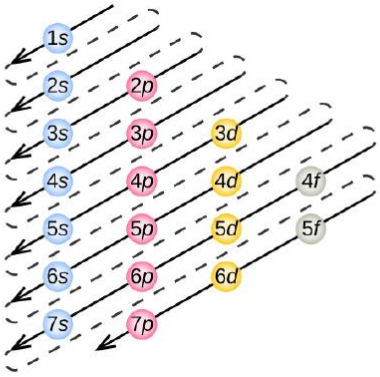



Figure **3.7.2**: The order of electron filling in an atom.

### Example 3.7.1: Electronic Configuration of Phosphorus Atoms

Using Figure **3.7.2** 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 3.7.1: Electronic Configuration of Chlorine Atoms

Using Figure **3.7.2** 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 $1s^2 2s^2 2p^6 3s^2 3p^5$.

Since the arrangement of the periodic table is based on the electron configurations, Figure **3.7.3** provides an alternative method for determining the electron configuration. The filling order simply **begins at the top left,** with hydrogen (Z=1) and includes each subshell as you proceed in increasing atomic number (*Z*) order.

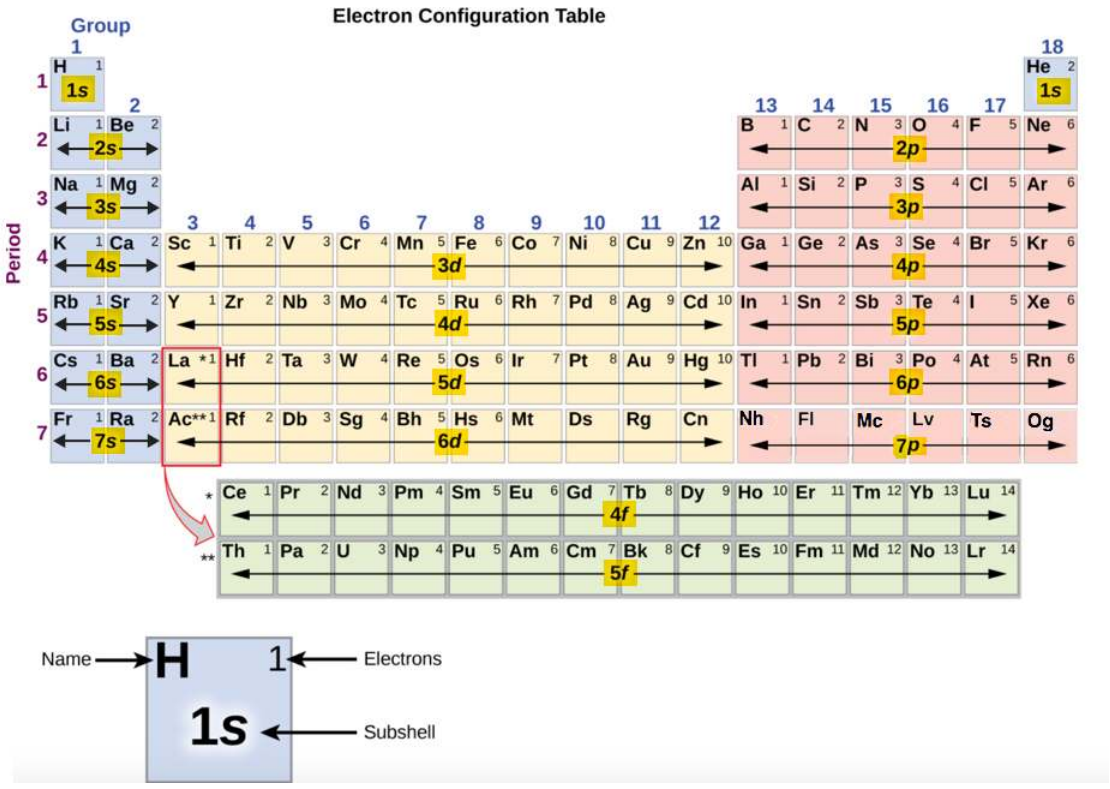



Figure **3.7.3**: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

For example, the first row (Period 1) contains H and He only, because only two electrons are required to fill the 1s subshell. The second row s-block, contains only two elements, Li and Be, to fill the 2s subshell. This is followed by the second row p-block, containing 6 elements (B through Ne) since six electrons are required to fill the 2p subshell. The third row is similar to the second row elements. Two electrons are needed (Na and Mg) to fill the 3s subshell and six electrons are required (Al through Ar) to complete the 3p subshell. After filling the 3*p* block up to Ar, we see the next subshell will be 4s (K, Ca), followed by the 3*d* subshell, which are filled by ten electrons (Sc through Zn). The 4p subshell is filled next by six electrons (Ga through Kr). As you can see, the periodic table shown in Figure **3.7.3** provides a simple way to remember the order of filling the subshells in determining the electron configuration. The order of filling subshells is the same: **1s, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5s, 4d, 5p, 6s,** etc.

### ✔ Example 3.7.2: Aluminum

Using Figure **3.7.3** as your guide, 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* **3.7.3**. 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 last one electron in the 3p subshell (**$3p^1$**).

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

### 3.7.2 Exercise

Using Figure **3.7.3** as your guide, write the electron configuration of the atom that has 20 electrons

**Answer**

*Start at Period 1 of Figure* **3.7.3**. 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 **$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$**

## Valence Electrons

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

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

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called **core electrons** ( Figure

\PageIndex4). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

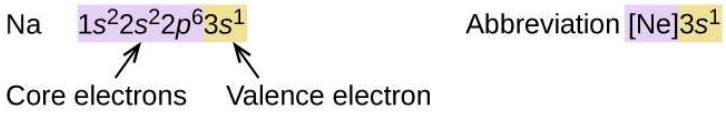



Figure **3.7.4**: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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

**Li : [He] $2s^1$**
**Na : [Ne] $3s^1$**

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

### Example 3.7.3

Examine the electron configuration of neutral phosphorus atoms in Example **3.7.1**, $1s^2 2s^2 2p^6 3s^2 3p^3$ and write the abbreviated notation.

#### Solution

Phosphorus has electron configuration, $1s^2 2s^2 2p^6 3s^2 3p^3$.

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

The 10 inner shell (core) electrons, $1s^2 2s^2 2p^6$ can be replaced by [Ne] (see Figure **3.7.3**). Abbreviated notation is : [Ne]$3s^2 3p^3$

### Exercise 3.7.3

Examine the electron configuration of neutral calcium atom (Exercise **3.7.2**), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, and write the abbreviated notation.

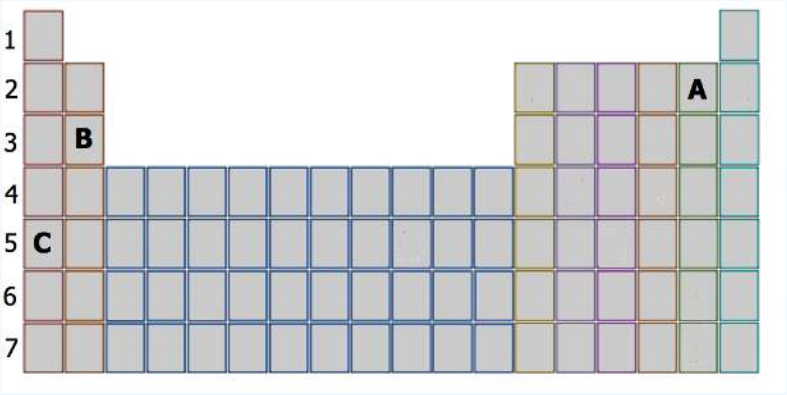
**Answer**

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

The 18 inner-shell (core) electrons, $1s^2 2s^2 2p^6 3s^2 3p^6$, can be replaced by [Ar], see Figure **3.7.3**. The abbreviated notation is: [Ar]$4s^2$

## Example 3.7.4

Based on their respective locations in the periodic table (use Figure **3.7.3**), determine the number of valence electrons and the valence shell configuration of elements A, B and C.




### Solution

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

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

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

## 3.7.4 Exercise

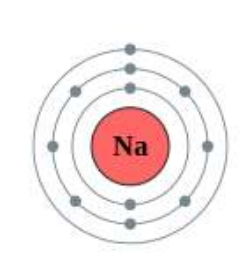
Using the location of Na is the periodic table (Figure **3.7.3**), draw the shell diagram of sodium atom.

**Answer**

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

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

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




## Concept Review Exercises

1. How are electrons organized in atoms?
2. What information does an electron configuration convey?

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

## Answers

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

## Key Takeaway

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

## Exercises

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# 3.8: 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 **3.8.1**. 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.

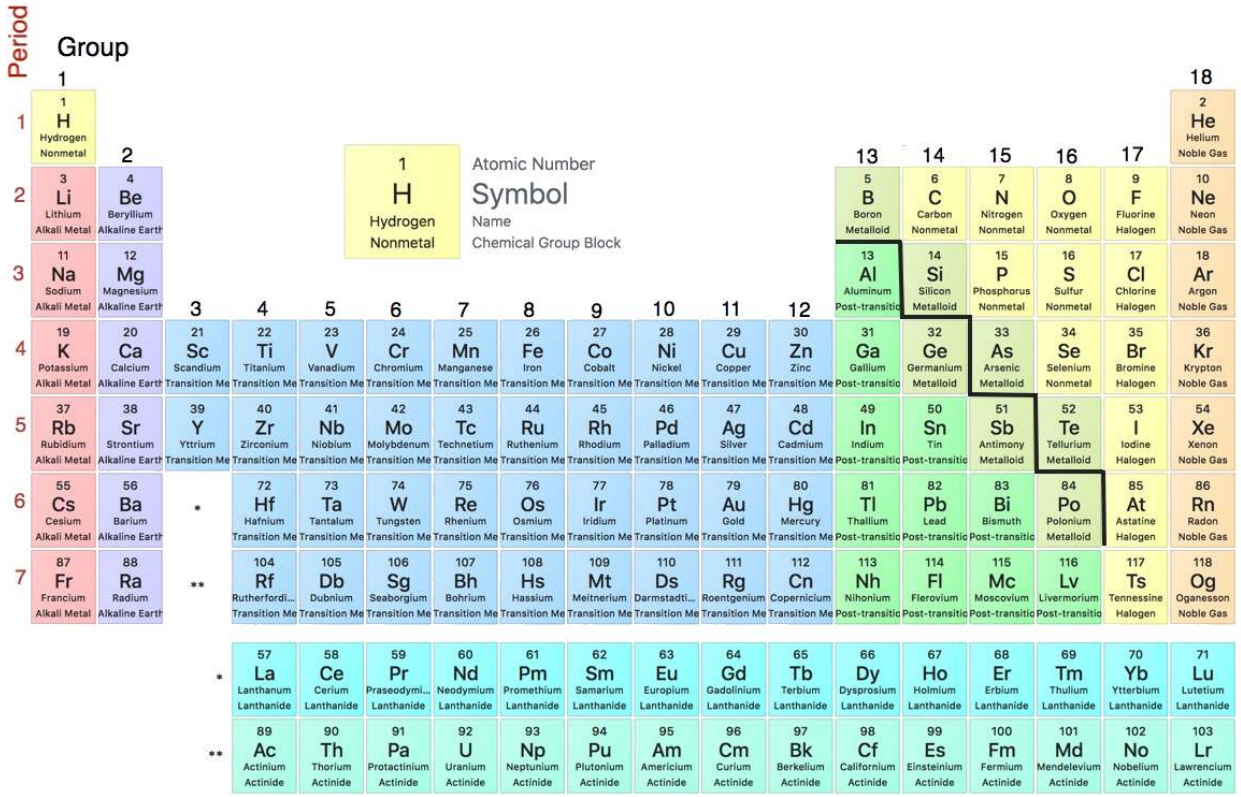



Figure **3.8.1**: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares).

## Features of the Periodic Table

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 **3.8.2**. 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 **3.8.2**, **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.

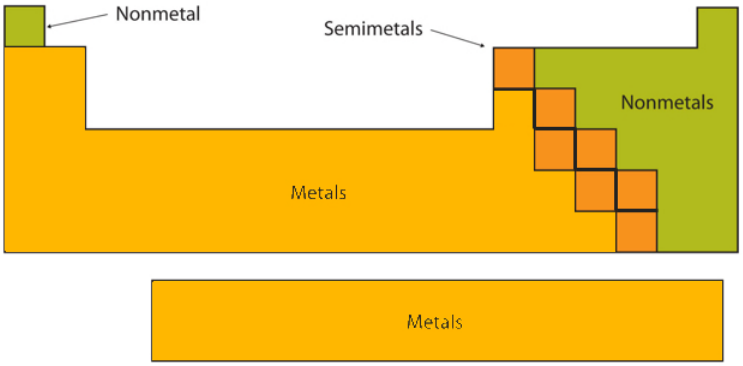



Figure **3.8.2**: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

**Example 3.8.1**

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

**Solution**

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.7.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

**3.8.1 Exercise**

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 **3.8.3**. The first two columns on the left and the last six columns on the right are called the **main group** or **representative** elements. The ten-column block between these columns 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**.

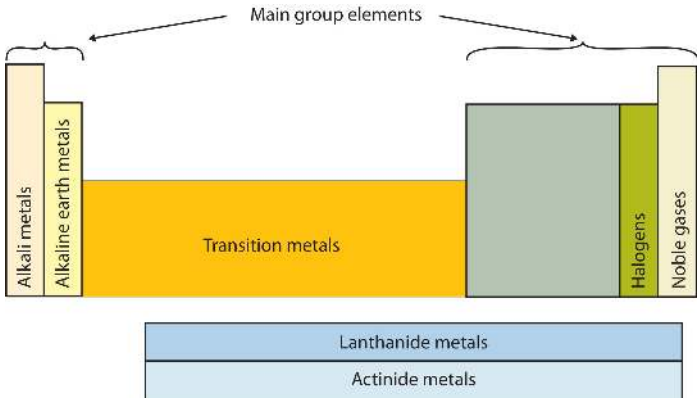



Figure **3.8.3**: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

Alkali metals are the first column. Alkaline earth metals are the second. Halogens are the second to last column. Noble gases are the last column.

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

Most of the elemental composition of the human body consists of main group elements. The first element appearing on the list that is not a 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. Transition metals have interesting chemical properties, partially because some of their electrons are in *d* subshells. 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 not listed explicitly in Table 2.1.2, so they are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

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

### Group 1: The Alkali Metals

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

### Group 2: The Alkaline Earth Metals

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

### Group 17: The Halogens

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

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

### Group 18: The Noble Gases

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

#### 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.

### Why do elements in a given group have similar properties?

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure **3.8.4**. Starting with the first

period and going from left to right, the table reproduces the order of filling of the electron subshells in atoms. Furthermore, elements in the same *group* share the same valence shell electron configuration. For example, all elements in the first column have a single *s* electron in their valence shells, so their electron configurations can be described as $ns^1$ (where *n* represents the shell number). This last observation is crucial. Chemistry is largely the result of interactions between the valence electrons of different atoms. Thus, atoms that have **the same valence shell electron configuration** will have **similar chemistry.**

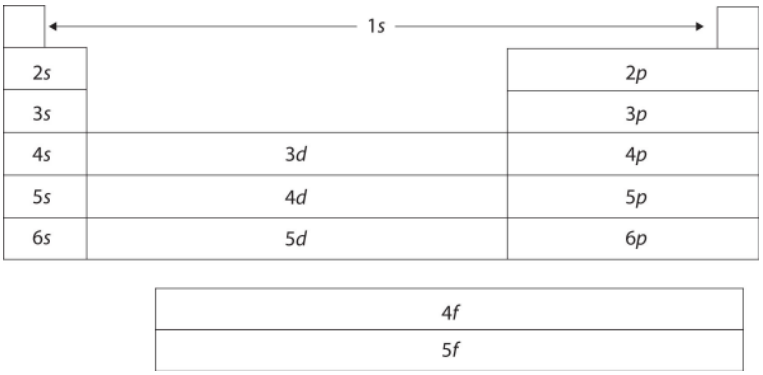



Figure **3.8.4** The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

## Example 3.8.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the alkaline earth metals
b. the column of elements headed by carbon

**Answer a**

The alkaline earth metals are in the second column of the periodic table. This column corresponds to the *s* subshell being filled with 2 electrons. Therefore, the valence shell electron configuration is $ns^2$.

**Answer b**

The electron configuration of carbon is $1s^22s^22p^2$. Its valence shell electron configuration is $2s^22p^2$. Every element in the same column should have a similar valence shell electron configuration, which we can represent as $ns^2np^2$.

## Exercise 3.8.1

Using the variable *n* to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the halogens
b. the column of elements headed by oxygen

**Answer a**

The halogens are in the 17th column (or Group 7A) of the periodic table. This column corresponds to the *p* subshell being filled with 5 electrons. Therefore, the valence shell electron configuration is $ns^2np^5$.

**Answer b**

The column headed by O is the 16th column (or Group 6A). This column corresponds to the *p* subshell being filled with 4 electrons. Therefore, the valence shell electron configuration is $ns^2np^4$.

## Valence Electrons and Group Number

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. With the exception of groups 3–12 (the transition metals), the units digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column.

Table **3.8.1**. The Group number and the number of valence electrons.

| Periodic table group | Valence electrons |
|---|---|
| Group 1 (I) (alkali metals) | 1 |
| Group 2 (II) (alkaline earth metals) | 2 |
| Groups 3-12 (transition metals) | 2* |
| Group 13 (III) (boron group) | 3 |
| Group 14 (IV) (carbon group) | 4 |
| Group 15 (V) (pnictogens) | 5 |
| Group 16 (VI) (chalcogens) | 6 |
| Group 17 (VII) (halogens) | 7 |
| Group 18 (VIII or 0) (noble gases) | 8** |

** The general method for counting valence electrons is generally not useful for transition metals.*

*** Except for helium, which has only two valence electrons.*

## Atomic Radius

The periodic table is useful for understanding atomic properties that show periodic trends. One such property is the atomic radius (Figure **3.8.5**). The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together. The units for atomic radii are picometers, equal to $10^{-12}$ meters. As an example, the internuclear distance between the two hydrogen atoms in an $\mathbf{H_2}$ molecule is measured to be $\mathbf{74\ pm}$. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = \mathbf{37\ pm}$.

As mentioned earlier, the higher the shell number, the farther from the nucleus the electrons in that shell are likely to be. In other words, the size of an atom is generally determined by the number of the valence electron shell. Therefore, as we go down a column on the periodic table, the atomic radius increases. As we go *across* a period on the periodic table, however, electrons are being added to the *same* valence shell; meanwhile, more protons are being added to the nucleus, so the positive charge of the nucleus is increasing. The increasing positive charge attracts the electrons more strongly, pulling them closer to the nucleus. Consequently, as we go across a period, from left to right, the atomic radius decreases. These trends are seen clearly in Figure **3.8.5**

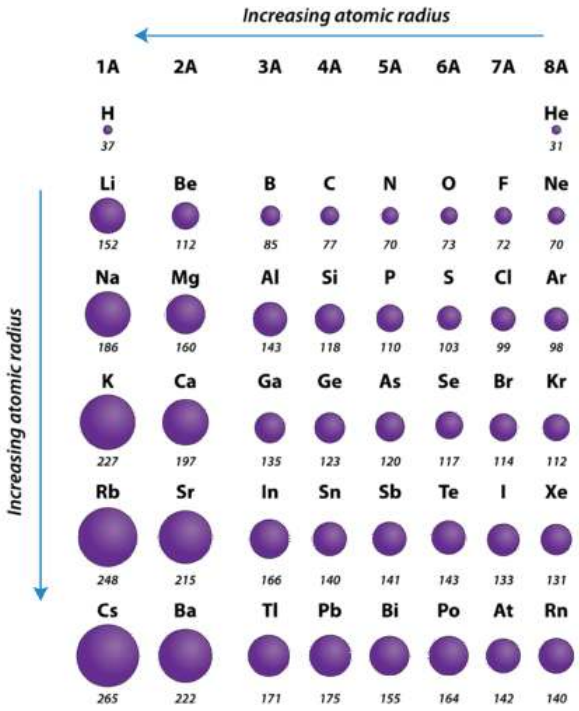



Figure **3.8.5** Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

### ✔ Example 3.8.2

Using the periodic table (rather than Figure **3.8.5**), which atom is larger?

a. N or Bi
b. Mg or Cl

**Answer a**

Bi is below N in Group 5A in the periodic table and has electrons in higher-numbered shells, hence we expect that Bi atoms are larger than N atoms.

**Answer b**

Both Mg and Cl are in period 3 of the periodic table, but Cl lies farther to the right. Therefore we expect Mg atoms to be larger than Cl atoms.

### ? Exercise 3.8.2

Using the periodic table (rather than Figure **3.8.5**), which atom is larger?

a. Li or F
b. Na or K

**Answer a**

Li and F are on the same period, but F lies farther to the right. Therefore, we expect Li to be larger than F atoms.

**Answer b**

K lies below Na in Group 1A, hence has more electron shells, making it larger than Na.

### Career Focus: Clinical Chemist

Clinical chemistry is the area of chemistry concerned with the analysis of body fluids to determine the health status of the human body. Clinical chemists measure a variety of substances, ranging from simple elements such as sodium and potassium to complex molecules such as proteins and enzymes, in blood, urine, and other body fluids. The absence or presence, or abnormally low or high amounts, of a substance can be a sign of some disease or an indication of health. Many clinical chemists use sophisticated equipment and complex chemical reactions in their work, so they not only need to understand basic chemistry, but also be familiar with special instrumentation and how to interpret test results.

## Concept Review Exercises

1. How are the elements organized into the periodic table?
2. Looking at the periodic table, where do the following elements appear?
    a. the metals
    b. the nonmetals
    c. the halogens
    d. the transition metals
    e. the noble gases
3. Describe the trends in atomic radii as related to an element's position on the periodic table.

## Answers

1. Elements are organized in order of increasing atomic number.
2. a. the left three-quarters of the periodic table (to the left of the zigzag band)
    b. the right quarter of the periodic table (to the right of the zigzag band)
    c. the next-to-last column of the periodic table
    d. the middle section of the periodic table
    e. the last column of the periodic table
3. As you go across the periodic table, atomic radii decrease; as you go down the periodic table, atomic radii increase.

## 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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# 3.S: Elements, Atoms, and the Periodic Table (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms and ask yourself how they relate to the topics in the chapter.*

An element is a substance that cannot be broken down into simpler chemical substances. Only about 90 naturally occurring elements are known. They have varying abundances on Earth and in the body. Each element has a one- or two-letter **chemical symbol**.

The **modern atomic theory** states that the smallest piece of an element is an **atom**. Individual atoms are extremely small, on the order of $10^{-10}$ m across. Most elements exist in pure form as individual atoms, but some exist as **diatomic molecules**. Atoms themselves are composed of subatomic particles. The **electron** is a tiny subatomic particle with a negative charge. The **proton** has a positive charge and, while small, is much larger than the electron. The **neutron** is also much larger than an electron but has no electrical charge.

Protons, neutrons, and electrons have a specific arrangement in an atom. The protons and neutrons are found in the center of the atom, grouped together into a **nucleus**. The electrons are found in fuzzy clouds around the nucleus.

Each element has a characteristic number of protons in its nucleus. This number of protons is the **atomic number** of the element. An element may have different numbers of neutrons in the nuclei of its atoms; such atoms are referred to as **isotopes**. Two isotopes of hydrogen are deuterium, with a proton and a neutron in its nucleus, and tritium, with a proton and two neutrons in its nucleus. The sum of the numbers of protons and neutrons in a nucleus is called the **mass number** and is used to distinguish isotopes from each other.

Masses of individual atoms are measured in **atomic mass units**. An atomic mass unit is equal to 1/12th of the mass of a single carbon-12 atom. Because different isotopes of an element have different masses, the **atomic mass** of an element is a weighted average of the masses of all the element's naturally occurring isotopes.

The modern theory of electron behavior is called **quantum mechanics**. According to this theory, electrons in atoms can only have specific, or **quantized**, energies. Electrons are grouped into general regions called **shells**, and within these into more specific regions called **subshells**. There are four types of subshells, and each type can hold up to a maximum number of electrons. The distribution of electrons into shells and subshells is the **electron configuration** of an atom. Chemistry typically occurs because of interactions between the electrons of the outermost shell of different atoms, called the valence shell electrons. Electrons in inner shells are called core electrons.

Elements are grouped together by similar chemical properties into a chart called the **periodic table**. Vertical columns of elements are called **groups** or **families**. Some of the groups of elements have names, like the alkali metals, the alkaline earth metals, the halogens, and the noble gases. A horizontal row of elements is called a **period**. Periods and groups have differing numbers of elements in them. The periodic table separates elements into **metals**, **nonmetals**, and **semimetals**. The periodic table is also separated into **main group elements**, **transition metals**, **lanthanide elements**, and **actinide elements**. The lanthanide and actinide elements are also referred to as **inner transition metal elements**. The shape of the periodic table reflects the sequential filling of shells and subshells in atoms.

The periodic table helps us understand trends in some of the properties of atoms. One such property is the **atomic radius** of atoms. From top to bottom of the periodic table, atoms get bigger because electrons are occupying larger and bigger shells. From left to right across the periodic table, electrons are filling the same shell but are being attracted by an increasing positive charge from the nucleus, and thus the atoms get smaller.

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# CHAPTER OVERVIEW

## 4: Ionic Bonding and Simple Ionic Compounds

There are only 118 known chemical elements but tens of millions of known chemical compounds. Compounds can be very complex combinations of atoms, but many important compounds are fairly simple. Table salt, as we have seen, consists of only two elements: sodium and chlorine. Nevertheless, the compound has properties completely different from either elemental sodium (a chemically reactive metal) or elemental chlorine (a poisonous, green gas). We will see additional examples of such differences in this chapter as we consider how atoms combine to form compounds.


4.1: Prelude to Ionic Bonding and Simple Ionic Compounds
4.2: Two Types of Bonding
4.3: Ions
4.4: Formulas for Ionic Compounds
4.5: Ionic Nomenclature
4.6: Formula Mass
4.7: Characteristics of Ionic Compounds
4.S: Ionic Bonding and Simple Ionic Compounds (Summary)


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# 4.1: Prelude to Ionic Bonding and Simple Ionic Compounds

We will see that the word salt has a specific meaning in chemistry, but to most people, this word refers to table salt. This kind of salt is used as a condiment throughout the world, but it was not always so abundant. Two thousand years ago, Roman soldiers received part of their pay as salt, which explains why the words salt and salary come from the same Latin root (salarium). Today, table salt is either mined or obtained from the evaporation of saltwater.

Table salt is sodium chloride (NaCl), which is a simple compound of two elements that are necessary for the human body to function properly. Sodium, for example, is important for nerve conduction and fluid balance. In fact, human blood is about a 0.9% sodium chloride solution, and a solution called normal saline is commonly administered intravenously in hospitals.

Although some salt in our diets is necessary to replenish the sodium and chloride ions that we excrete in urine and sweat, too much is unhealthy, and many people may be ingesting more salt than their bodies need. The RDI of sodium is 2,400 mg—the amount in about 1 teaspoon of salt—but the average intake of sodium in the United States is between 4,000 mg and 5,000 mg, partly because salt is a common additive in many prepared foods. Previously, the high ingestion of salt was thought to be associated with high blood pressure, but current research does not support this link. Even so, some doctors still recommend a low-salt diet (never a “no-salt” diet) for patients with high blood pressure, which may include using a salt substitute. Most salt substitutes use potassium instead of sodium, but some people complain that the potassium imparts a slightly bitter taste.

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# 4.2: Two Types of Bonding

**Learning Objectives**

- Define the octet rule.
- Describe how ionic bonds are formed.

Atoms can join together by forming a chemical bond, which is a very strong attraction between two atoms. Chemical bonds are formed when electrons in different atoms interact with each other to make an arrangement that is more stable than when the atoms are apart.

What causes atoms to make a chemical bond with other atoms, rather than remaining as individual atoms? A clue comes by considering the noble gas elements, the rightmost column of the periodic table. These elements—helium, neon, argon, krypton, xenon, and radon—do not form compounds very easily, which suggests that they are especially stable as lone atoms. What else do the noble gas elements have in common? Except for helium, they all have eight valence electrons. Chemists have concluded that atoms are especially stable if they have eight electrons in their outermost shell. This useful rule of thumb is called the **octet rule**, and it is a key to understanding why compounds form.

> *Of the noble gases, only krypton, xenon, and radon have been found to make compounds.*

There are two ways for an atom that does not have an octet of valence electrons to obtain an octet in its outer shell. One way is the transfer of electrons between two atoms until all atoms have octets. Because some atoms will lose electrons and some atoms will gain electrons, there is no overall change in the number of electrons, but individual atoms acquire a nonzero electric charge. Those that lose electrons become positively charged, and those that gain electrons become negatively charged. Charged atoms are called ions. Because opposite charges attract (while like charges repel), these oppositely charged ions attract each other, forming **ionic bonds**. The resulting compounds are called **ionic compounds** and are the primary subject of this chapter.

The second way for an atom to obtain an octet of electrons is by sharing electrons with another atom. These shared electrons simultaneously occupy the outermost shell of more than one atom. The bond made by electron sharing is called a **covalent bond**.

Despite our focus on the octet rule, we must remember that for small atoms, such as hydrogen, helium, and lithium, the first shell is, or becomes, the outermost shell and hold only two electrons. Therefore, these atoms satisfy a "**duet rule**" rather than the octet rule.

**Example 4.2.1**

A sodium atom has one valence electron. Do you think it is more likely for a sodium atom to lose one electron or gain seven electrons to obtain an octet?

**Solution**

Although either event is possible, a sodium atom is more likely to lose its single valence electron. When that happens, it becomes an ion with a net positive charge. This can be illustrated as follows:

| Sodium atom | | Sodium ion | |
|---|---|---|---|
| 11 protons | 11+ | 11 protons | 11+ |
| 11 electrons | 11− | 10 electrons | 10− |
| | 0 overall charge | | +1 overall charge |

**Exercise 4.2.1**

A fluorine atom has seven valence electrons. Do you think it is more likely for a fluorine atom to lose seven electrons or gain one electron to obtain an octet? Write the formula of the resulting ion.

**Answer**

The process that involves less number of electrons is more favorable. Fluorine would gain one electron. The formula of the resulting ion is $F^-$.

## Key Takeaways

- Atoms have a tendency to have eight electrons in their valence shell.
- The attraction of oppositely charged ions is what makes ionic bonds.

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# 4.3: Ions

**Learning Objectives**

- Define the two types of ions.
- Use Lewis diagrams to illustrate ion formation.

Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while some atoms lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge as a result because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called cations. Most metals become cations when they make ionic compounds.

Some atoms have nearly eight electrons in their valence shell and can gain additional valence electrons until they have an octet. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called anions. Most nonmetals become anions when they make ionic compounds.

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

## Electron Transfer

We can use electron configurations to illustrate the electron transfer process between sodium atoms and chlorine atoms.

Na: 2,8,1

As demonstrated here, a sodium atom (Na) has one valence electron in the third principal energy level. It is likely to achieve an octet in its outermost shell by losing its one valence electron. The cation produced in this way, $Na^+$, is called the sodium ion to distinguish it from the element. The sodium ion, $Na^+$, has the electron configuration with an octet of electrons from the second principal energy level. It is now the same as that of the noble gas neon. The term **isoelectronic** refers to an atom and an ion of a different atom (or two different ions) that have the same electron configuration. The sodium ion is isoelectronic with the neon atom. The equation below illustrates this process.

$$\begin{array}{ccc} \mathbf{Na} & \rightarrow & \mathbf{Na^+ + e^-} \\ \mathbf{2\,8\,1} & & \mathbf{2\,8\ (octet)} \end{array} \tag{4.3.1}$$

Figure **4.3.1** is a graphical depiction of this process.

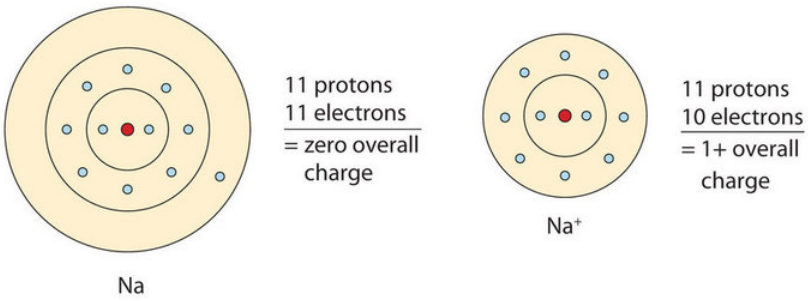



Figure **4.3.1**: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

Now, let's consider chlorine atom, Cl: 2,8,7

Only one more electron is needed to achieve an octet in chlorine's valence shell. When a chlorine atom gains an electron, its outermost principal energy level achieves an octet. In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, $Cl^-$, is called the chloride ion;

note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion. This process is illustrated below. (In table salt, this electron comes from the sodium atom.)

$$\begin{array}{ccc} Cl + e^- & \rightarrow & Cl^- \\ 2\,8\,7 & & 2\,8\,8(\text{octet}) \end{array} \tag{4.3.2}$$

Figure **4.3.2** is a graphical depiction of this process.

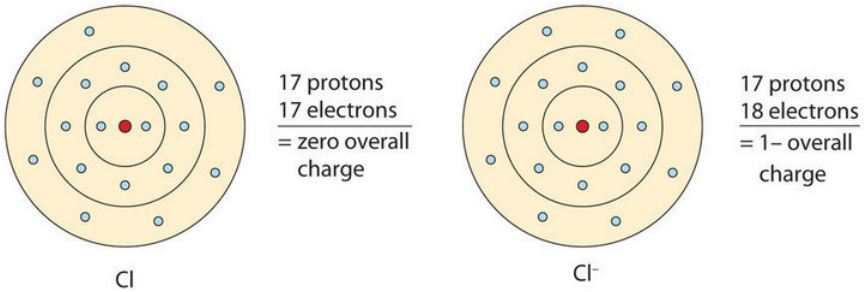



Figure **4.3.2**: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

With two oppositely charged ions, there is an electrostatic attraction between them because opposite charges attract. The resulting combination is the compound sodium chloride. Notice that there are no leftover electrons. The number of electrons lost by the sodium atom (one) equals the number of electrons gained by the chlorine atom (one), so the compound is electrically neutral. In macroscopic samples of sodium chloride, there are billions and billions of sodium and chloride ions, although there is always the same number of cations and anions.

**Example 4.3.1**

Write the electron configuration of aluminum atom (Z=13). How many electrons must Al lose/gain to achieve octet? Write the formula of the resulting ion and its electron configuration.

**Solution**

The electron configuration of Al atom is 2,8,3. The second shell has octet (8) while the valence shell has 3 electrons. Al can achieve octet by losing the 3 valence electrons. The resulting cation is $Al^{3+}$ with electron configuration, 2,8.

**Exercise 4.3.1**

Write the electron configuration of oxygen atom (Z=8). How many electrons must O lose/gain to achieve octet? Write the formula of the resulting ion and its electron configuration.

**Answer**

The electron configuration of O atom is 2,6. The second shell has six electrons and needs two electrons to achieve octet. Oxygen will gain 2 electrons. The resulting anion is $O^{2-}$ with electron configuration, 2,8.

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, 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 **4.3.3** shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a multiply charged ion. The barium cation is written $Ba^{2+}$, not $Ba^{+2}$.

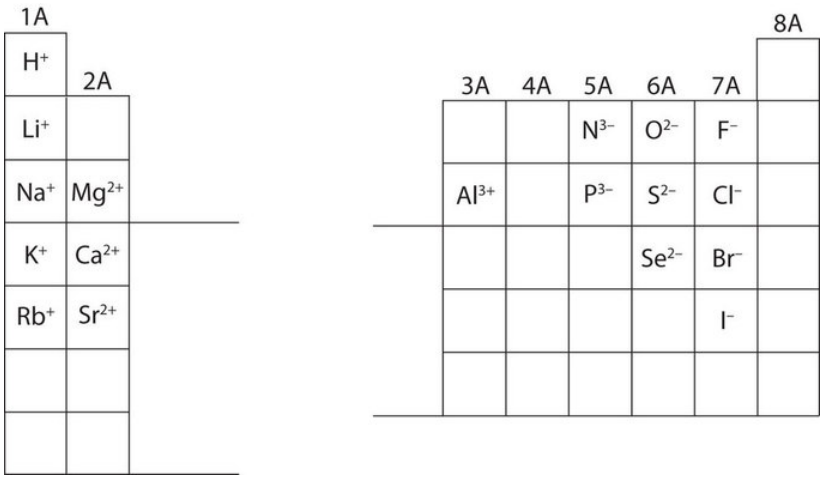



Figure **4.3.3**: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

**Example 4.3.2**

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.

**Exercise 4.3.2**

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.

## Lewis Diagrams

Chemists use simple diagrams to show an atom's valence electrons and how they transfer. These diagrams have two advantages over the electron shell diagrams. First, they show only valence electrons. Second, instead of having a circle around the chemical symbol to represent the electron shell, they have up to eight dots around the symbol; each dot represents a valence electron. These dots are arranged to the right and left and above and below the symbol, **with no more than two dots on a side**. For example, the representation for sodium is as follows:




and the representation for chlorine is as follows:




For the above diagrams, it does not matter what sides the dots are placed on in Lewis diagrams as long as each side has a maximum of two dots.

These diagrams are called **Lewis electron dot diagrams**, or simply Lewis diagrams, after Gilbert N. Lewis, the American chemist who introduced them. To write an element's Lewis dot symbol, place the dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. In other words, **place the dots singly on each side before pairing them**. The Lewis electron dot diagram of fluorine, for example, with seven valence electrons, is constructed as follows:

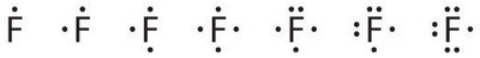
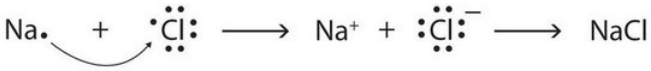


Figure **4.3.4** shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the **main group** elements, the **number of valence electrons** is the **same as the group number** listed at the top of the periodic table.



Figure **4.3.4**: Lewis Electron Dot Diagrams of the Elements Lithium through Neon

The transfer of electrons can be illustrated easily with Lewis diagrams:



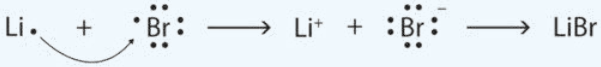
In representing the final formula, the dots are omitted.

**Example 4.3.3**

Starting with lithium and bromine atoms, use Lewis diagrams to show the formation of the ionic compound LiBr.

**Solution**

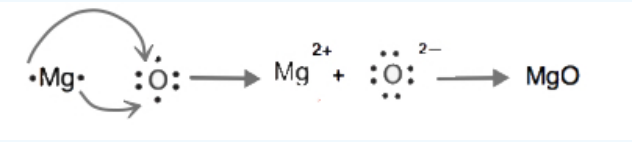
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it will have the same Lewis diagram that chlorine has. Therefore,



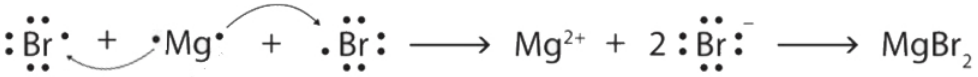
**Exercise 4.3.3**

Starting with magnesium and oxygen atoms, use Lewis diagrams to show the formation of the ionic compound MgO.

**Answer**



Some ionic compounds have different numbers of cations and anions. In those cases, electron transfer occurs between more than one atom. For example, here is the formation of $MgBr_2$:



Notice that in this example there are two bromide ions (1– charge) needed for every one magnesium ion (2+ charge) in order for the overall charge of the compound to equal zero. This is called **charge balance**. The number of each type of ion is indicated in the formula by the subscript.

Most of the elements that make ionic compounds form an ion that has a characteristic charge. For example, sodium makes ionic compounds in which the sodium ion always has a 1+ charge. Chlorine makes ionic compounds in which the chloride ion always has a 1− charge. Some elements, especially transition metals, can form ions of multiple charges. Figure **4.3.5** shows the characteristic charges for some of these ions. As we saw in Figure **4.3.1**, there is a pattern to the charges on many of the main group ions, but there is no simple pattern for transition metal ions (or for the larger main group elements).

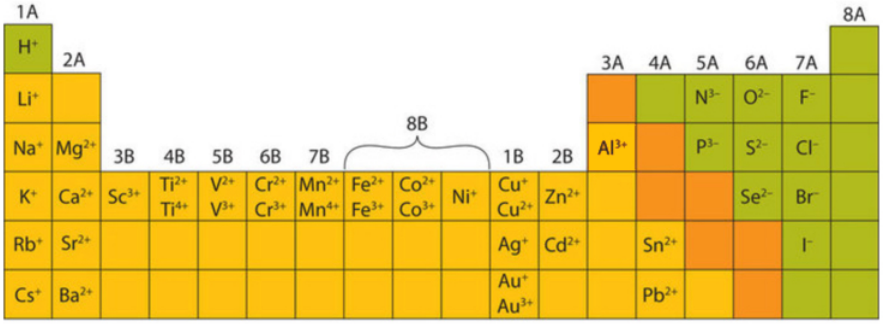



Figure **4.3.5**: Charges of the Monatomic Ions. Note that some atoms commonly form ions of variable charges.

## Key Takeaways

- Ions can be positively charged or negatively charged.
- A Lewis diagram is used to show how electrons are transferred to make ions and ionic compounds.

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# 4.4: Formulas for Ionic Compounds

**Learning Objectives**

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

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

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 4.4.1). As you can see, there are no individual NaCl "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use NaCl (one Na symbol and one Cl symbol) to represent the compound. Thus, NaCl is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that NaCl crystals are composed of individual NaCl units, Figure 4.4.1 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

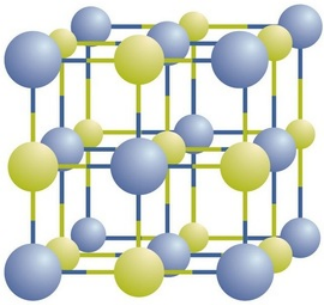


Figure 4.4.1: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

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

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

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

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

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

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

$$Mg^{2+}Cl^{-} \tag{4.4.1}$$

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

$$Mg^{2+}\ Cl^{-}\ Cl^{-} \tag{4.4.2}$$

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

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

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

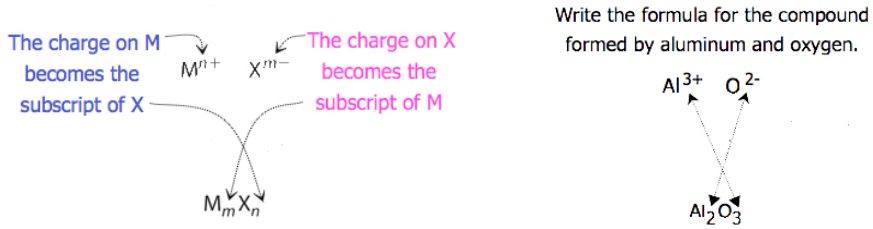



Figure **4.4.2**: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

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

**Example 4.4.1**

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

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

**Solution**

a. To obtain a valence shell octet, sodium forms an ion with a 1+ charge, while the sulfur ion has a 2− charge. Two sodium 1+ ions are needed to balance the 2− charge on the sulfur ion. Rather than writing the formula as **NaNaS**, we shorten it by convention to **$Na_2S$**.
b. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1− charge. Three fluorine 1− ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as **$AlF_3$**.
c. Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxygen atom has a 2− charge as an ion. To balance the positive and negative charges, we look to the least common multiple—6: two iron 3+ ions will give 6+, while three 2− oxygen ions will give 6−, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is **$Fe_2O_3$**. Alternatively, use the crossing charges method shown in Figure 3.3.2.

**Exercise 4.4.1**

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

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

**Answer a:**

CaO

**Answer b:**

CuS

**Answer c:**

$Cu_2S$

## 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 Lewis structures, names and formulas of some polyatomic ions are found in Table 3.3.1.

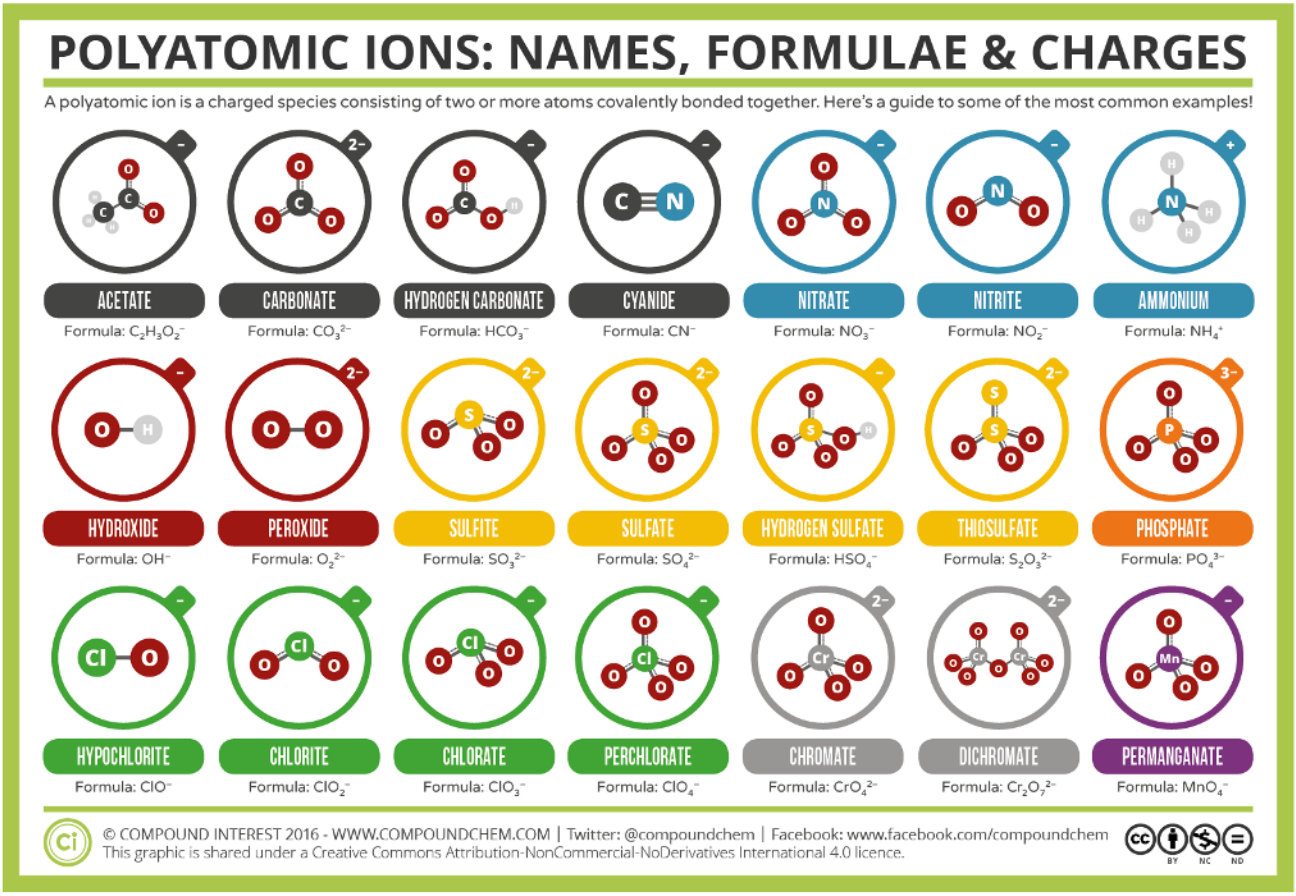



***Table* 4.4.1:** *Some Polyatomic Ions*

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table **4.4.2** 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. Figure **4.4.2** lists the most common polyatomic ions.

Table **4.4.2**: Ion Names and Ion Formulas of Common Polyatomic Ions


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| Ion Name | Ion Formula |
| --- | --- |
| ammonium ion | $NH_4^{+1}$ |
| hydroxide ion | $OH^{-1}$ |
| cyanide ion | $CN^{-1}$ |
| carbonate ei | $CO_3^{-2}$ |

| Ion Name | Ion Formula |
| --- | --- |
| bicarbonate or hydrogencarbonate | $HCO_3^-$ |
| acetate ion | $C_2H_3O_2^{-1}$ **or** $CH_3CO_2^{-1}$ |
| n | $NO_3^{-1}$ |

| Ion Name | Ion Formula |
| --- | --- |
| itrate ion | |
| nitrite ion | $NO_2^{-1}$ |
| sulfate ion | $SO_4^{-2}$ |
| sulfite ion | $SO_3^{-2}$ |
| phos | $PO_4^{-3}$ |

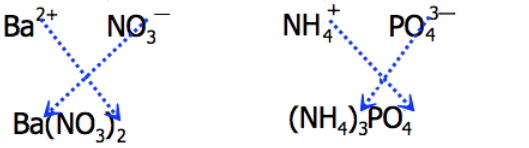
| Ion Name | Ion Formula |
|---|---|
| phate ion | |
| phosphite ion | $PO_3^{-3}$ |

Note that only one polyatomic ion in this Table, the ammonium ion ($NH_4^{+1)}$, is a cation. This polyatomic ion contains one nitrogen and four hydrogens that collectively bear a +1 charge. 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 particles. 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. As has been repeatedly emphasized in several sections of this text, no two chemical formulas should share a common chemical name. 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, the nitrate ion, which is symbolized as $NO_3^{-1}$, has one more oxygen than the nitrite ion, which is symbolized as $NO_2^{-1}$. However, the sulfate ion is symbolized as $SO_4^{-2}$. While both the nitrate ion and the sulfate ion share an "-ate" suffix, the former contains three oxygens, but 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.

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

Write the formula for the compound formed by

a. barium and nitrate b. ammonium and phosphate




**Example 4.4.2**

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

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

**Solution**

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

**Exercise 4.4.2**

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

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

**Answer a:**

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

**Answer b:**

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

## Recognizing Ionic Compounds

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

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

**Example 4.4.3**

Identify each compound as ionic or not ionic.

a. $\mathbf{Na_2O}$
b. $\mathbf{PCl_3}$

c. $NH_4Cl$
d. $OF_2$

**Solution**

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

**Exercise 4.4.3**

Identify each compound as ionic or not ionic.

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

**Answer a:**

not ionic

**Answer b:**

ionic

**Answer c:**

ionic

**Answer d:**

not ionic

**Looking Closer: Blood and Seawater**

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

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

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

## Key Takeaways

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

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# 4.5: Ionic Nomenclature

**Learning Objectives**

- To use the rules for naming ionic compounds

After learning a few more details about the names of individual ions, you will be 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 Ions

The name of a monatomic cation is simply the name of the element followed by the word *ion*. Thus, $Na^+$ is the sodium ion, $Al^{3+}$ is the aluminum ion, $Ca^{2+}$ is the calcium ion, and so forth.

We have seen that some elements lose different numbers of electrons, producing ions of different charges. Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish $Fe^{2+}$ from $Fe^{3+}$. The same issue arises for other ions with more than one possible charge.

There are two ways to make this distinction. In the simpler, more modern approach, called the ***Stock system***, an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word *ion*. Thus, $Fe^{2+}$ is called the iron(II) ion, while $Fe^{3+}$ is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the $Na^+$ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

Table **4.5.1**: The Common System of Cation Names

| Element | Stem | Charge | Name |
|---|---|---|---|
| iron | ferr- | 2+ | ferrous ion |
| | | 3+ | ferric ion |
| copper | cupr- | 1+ | cuprous ion |
| | | 2+ | cupric ion |
| tin | stann- | 2+ | stannous ion |
| | | 4+ | stannic ion |
| lead | plumb- | 2+ | plumbous ion |
| | | 4+ | plumbic ion |
| chromium | chrom- | 2+ | chromous ion |
| | | 3+ | chromic ion |
| gold | aur- | 1+ | aurous ion |
| | | 3+ | auric ion |

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table **4.5.1** lists the elements that use the common system, along with their respective cation names.

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 **4.5.2** lists the names of some common monatomic ions.

Table **4.5.2**: Some Monatomic Anions

| Ion | Name |
|---|---|
| $F^-$ | fluoride ion |
| $Cl^-$ | chloride ion |
| $Br^-$ | bromide ion |
| $I^-$ | iodide ion |
| $O^{2-}$ | oxide ion |
| $S^{2-}$ | sulfide ion |
| $P^{3-}$ | phosphide ion |
| $N^{3-}$ | nitride ion |

The polyatomic ions have their own characteristic names, as discussed earlier.

**Example 4.5.1**

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 **4.5.2** )

**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 4.5.1**

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 4.5.2

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 4.5.2

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**

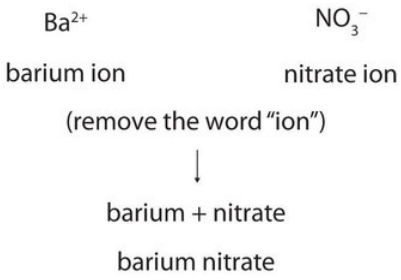
$Fe^{2+}$

**Answer d**

$K^+$

## Naming Compounds

Now that we know how to name ions, we are ready to name ionic compounds. We do so 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 $\mathbf{Ba(NO_3)_2}$?




The compound's name does not indicate that there are two nitrate ions for every barium ion. You must determine the relative numbers of ions by balancing the positive and negative charges.

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $\mathbf{FeCl_2}$ and $\mathbf{FeCl_3}$. In the first compound, the iron ion has a 2+ charge because there are two $\mathbf{Cl^-}$ 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 $\mathbf{Cl^-}$ 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.

### Example 4.5.3

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 4.5.3**

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

Figure 4.5.1 is a synopsis of how to name simple ionic compounds.

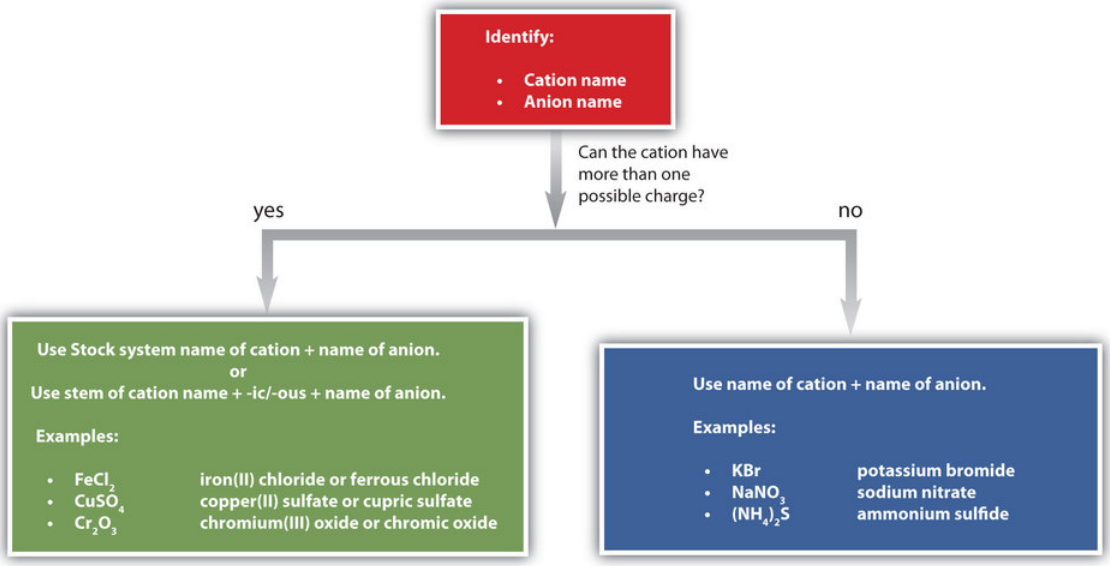



Figure 4.5.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

## KEY TAKEAWAY

- Each ionic compound has its own unique name that comes from the names of the ions.

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# 4.6: Formula Mass

**Learning Objectives**

- To determine the formula mass of an ionic compound.

One skill needed in future chapters is the ability to determine the mass of the formula of an ionic compound. This quantity is called the formula mass. The formula mass is obtained by adding the masses of each individual atom in the formula of the compound. Because a proper formula is electrically neutral (with no net electrons gained or lost), the ions can be considered atoms for the purpose of calculating the formula mass.

Let us start by calculating the formula mass of sodium chloride (NaCl). This formula mass is the sum of the atomic masses of one sodium atom and one chlorine atom, which we find from the periodic table; here, we use the masses to two decimal places:

Table shows how to calculate the formula mass of sodium chloride by using their atomic masses.

| | |
|---|---|
| Na: | 22.99 amu |
| Cl: | + 35.45 amu |
| Total: | 58.44 amu |

To two decimal places, the formula mass of NaCl is 58.44 amu.

When an ionic compound has more than one anion or cation, you must remember to use the proper multiple of the atomic mass for the element in question. For the formula mass of calcium fluoride ($CaF_2$), we must multiply the mass of the fluorine atom by 2 to account for the two fluorine atoms in the chemical formula:

Table shows how to find the formula mass of calcium fluoride by using their atomic masses.

| | | |
|---|---|---|
| Ca: | 1 × 40.08 | 40.08 amu |
| F: | 2 × 19.00 = | + 38.00 amu |
| Total: | | 78.08 amu |

The formula mass of $CaF_2$ is 78.08 amu.

For ionic compounds with polyatomic ions, the sum must include the number and mass of each atom in the formula for the polyatomic ion. For example, potassium nitrate ($KNO_3$) has one potassium atom, one nitrogen atom, and three oxygen atoms:

Table shows how to find the formula mass of potassium nitrate by using their atomic masses.

| | | |
|---|---|---|
| K: | 1 × 39.10 | 39.10 amu |
| N: | 1 × 14.01 | + 14.01 amu |
| O: | 3 × 16.00 = | + 48.00 amu |
| Total: | | 101.11 amu |

The formula mass of $KNO_3$ is 101.11 amu.

> Potassium nitrate is a key ingredient in gunpowder and has been used clinically as a diuretic.

When a formula contains more than one polyatomic unit in the chemical formula, as in $Ca(NO_3)_2$, do not forget to multiply the atomic mass of every atom inside the parentheses by the subscript outside the parentheses. This is necessary because the subscript refers to the *entire polyatomic ion*. Thus, for $Ca(NO_3)_2$, the subscript 2 implies two complete nitrate ions, so we must sum the masses of two (1 × 2) nitrogen atoms and six (3 × 2) oxygen atoms, along with the mass of a single calcium atom:

Table shows how to find the formula mass of $Ca(NO_3)_2$ by using their atomic masses.

| | | |
|---|---|---|
| Ca: | 1 × 40.08 | 40.08 amu |
| N: | 2 × 14.01 = | + 28.02 amu |
| O: | 6 × 16.00 = | + 96.00 amu |
| Total: | | 164.10 amu |

The key to calculating the formula mass of an ionic compound is to correctly count each atom in the formula and multiply the atomic masses of its atoms accordingly.

The Periodic Table is found in this link: Periodic Table of Elements with Atomic Mass [pubchem.ncbi.nlm.nih.gov]

## Example 4.6.1

Use the atomic masses (**rounded to two decimal places**) from the **Periodic Table** to determine the formula mass for each ionic compound.

a. $FeCl_3$
b. $(NH_4)_3PO_4$

### Solution

a.

Table shows how to find the formula mass of $FeCl_3$ by using their atomic masses.

| | | |
|---|---|---|
| Fe: | | 55.84 amu |
| Cl: | 3 × 35.45 = | + 106.35 amu |
| Total: | | 162.19 amu |

The formula mass of $FeCl_3$ is 162.19 amu.

a. When we distribute the subscript 3 through the parentheses containing the formula for the ammonium ion, we see that we have 3 nitrogen atoms and 12 hydrogen atoms. Thus, we set up the sum as follows:

Table shows how to find the formula mass of $(NH_4)_3PO_4$ by using their atomic masses.

| | | |
|---|---|---|
| N: | 3 × 14.01 = | 42.03 amu |
| H: | 12 × 1.01 = | + 12.12 amu |
| P: | | + 30.97 amu |
| O: | 4 × 16.00 = | + 64.00 amu |
| Total: | | 149.12 amu |

The formula mass for $(NH_4)_3PO_4$ is 149.12 amu.

## Exercise 4.6.1

Use the atomic masses (**rounded to two decimal places**) from the **Periodic Table** to determine the formula mass for each ionic compound.

a. $TiO_2$
b. AgBr
c. $Au(NO_3)_3$

d. $Fe_3(PO_4)_2$

**Answer a:**

47.87 + 2 (16.00) = 79.87 amu

**Answer b:**

107.87 + 79.90 = 187.77 amu

**Answer c:**

196.97 + 3(14.01) + 9(16.00) = 383.00 amu

**Answer d:**

3(55.84) + 2(30.97) + 8(16.00) = 357.46 amu

## To Your Health: Hydrates

Some ionic compounds have water ($H_2O$) incorporated within their formula unit. These compounds, called *hydrates*, have a characteristic number of water units associated with each formula unit of the compound. Hydrates are solids, not liquids or solutions, despite the water they contain.

To write the chemical formula of a hydrate, write the number of water units per formula unit of compound after its chemical formula. The two chemical formulas are separated by a vertically centered dot. The hydrate of copper(II) sulfate has five water units associated with each formula unit, so it is written as $CuSO_4 \cdot 5H_2O$. The name of this compound is copper(II) sulfate pentahydrate, with the *penta-* prefix indicating the presence of five water units per formula unit of copper(II) sulfate.



*Magnesium sulfate heptahydrate. (Public Domain; Chemicalinterest).*

Hydrates have various uses in the health industry. Calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$), known as plaster of Paris, is used to make casts for broken bones. Epsom salt ($MgSO_4 \cdot 7H_2O$) is used as a bathing salt and a laxative. Aluminum chloride hexahydrate is an active ingredient in antiperspirants. The accompanying table lists some useful hydrates.

Table **4.6.1**: Names and Formulas of Some Widely Used Hydrates

| Formula | Name | Uses |
|---|---|---|
| $AlCl_3 \cdot 6H_2O$ | aluminum chloride hexahydrate | antiperspirant |
| $CaSO_4 \cdot \frac{1}{2}H_2O$ | calcium sulfate hemihydrate (plaster of Paris) | casts (for broken bones and castings) |
| $CaSO_4 \cdot 2H_2O$ | calcium sulfate dihydrate (gypsum) | drywall component |
| $CoCl_2 \cdot 6H_2O$ | cobalt(II) chloride hexahydrate | drying agent, humidity indicator |
| $CuSO_4 \cdot 5H_2O$ | copper(II) sulfate pentahydrate | fungicide, algicide, herbicide |
| $MgSO_4 \cdot 7H_2O$ | magnesium sulfate heptahydrate (Epsom salts) | laxative, bathing salt |
| $Na_2CO_3 \cdot 10H_2O$ | sodium carbonate decahydrate (washing soda) | laundry additive/cleaneKEY TAKEAWAY |

## KEY TAKEAWAY

- Formula masses of ionic compounds can be determined from the masses of the atoms in their formulas.

## EXERCISES

1. What is the relationship between atomic mass and formula mass?

2. How are subscripts used to determine a formula mass when more than one polyatomic ion is present in a chemical formula?

3. What is the formula mass for the ionic compound formed by each pair of ions?

   a. $Na^+$ and $Br^-$
   b. $Mg^{2+}$ and $Br^-$
   c. $Mg^{2+}$ and $S^{2-}$

4. What is the formula mass for the ionic compound formed by each pair of ions?

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

5. What is the formula mass for the ionic compound formed by each pair of ions?

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

6. What is the formula mass for the ionic compound formed by each pair of ions?

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

7. What is the formula mass for each compound?

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

8. What is the formula mass for each compound?

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

9. What is the formula mass for each compound?

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

10. What is the formula mass for each compound?

    a. $NH_4NO_3$
    b. $K_2Cr_2O_7$
    c. $Cu_2CO_3$
    d. $NaHCO_3$

11. What is the formula mass for each compound?

    a. $Al(HSO_4)_3$
    b. $Mg(HSO_4)_2$

12. What is the formula mass for each compound?

    a. $Co(HCO_3)_2$
    b. $LiHCO_3$

## Answers

1. The formula mass is the sum of the atomic masses of the atoms in the formula.
2. The subscript is distributed throughout the parentheses to determine the total number of atoms in the formula.

3.

    a. 102.89 amu
    b. 184.11 amu
    c. 56.38 amu

4.

    a. 74.55 amu
    b. 95.21 amu
    c. 103.28 amu

5.

    a. 82.98 amu
    b. 100.95 amu
    c. 150.17 amu

6.

    a. 35.01 amu
    b. 134.87 amu
    c. 51.79 amu

7.

    a. 295.55 amu
    b. 215.65 amu
    c. 490.15 amu
    d. 426.01 amu

8.

    a. 152.00 amu
    b. 68.00 amu
    c. 278.10 amu
    d. 349.00 amu

9.

    a. 238.03 amu
    b. 357.49 amu
    c. 156.08 amu
    d. 78.01 amu

10.

    a. 80.06 amu

b. 294.20 amu
c. 187.11 amu
d. 84.01 amu

11.

a. 318.22 amu
b. 218.47 amu

12.

a. 180.97 amu
b. 67.96 amu

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# 4.7: Characteristics of Ionic Compounds

**Learning Objectives**

- To describe the 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.

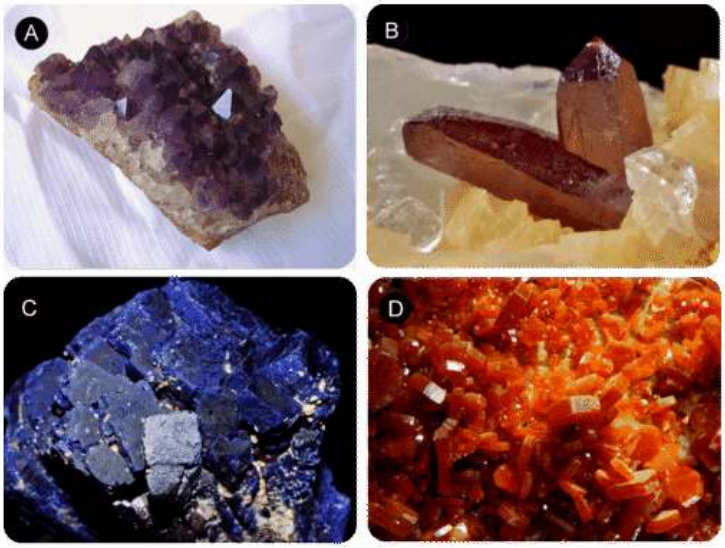



Figure 3.6.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz, $SiO_2$, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral, $Cu_3(CO_3)_2(OH)_2$. (D) Vanadinite - the primary ore of vanadium, $Pb_3(VO_4)_3Cl$.*

## Physical Properties of Ionic Compounds

### 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°C. 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.

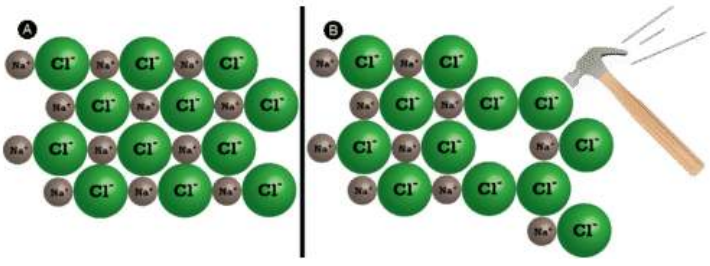



Figure 3.6.2: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

## 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.

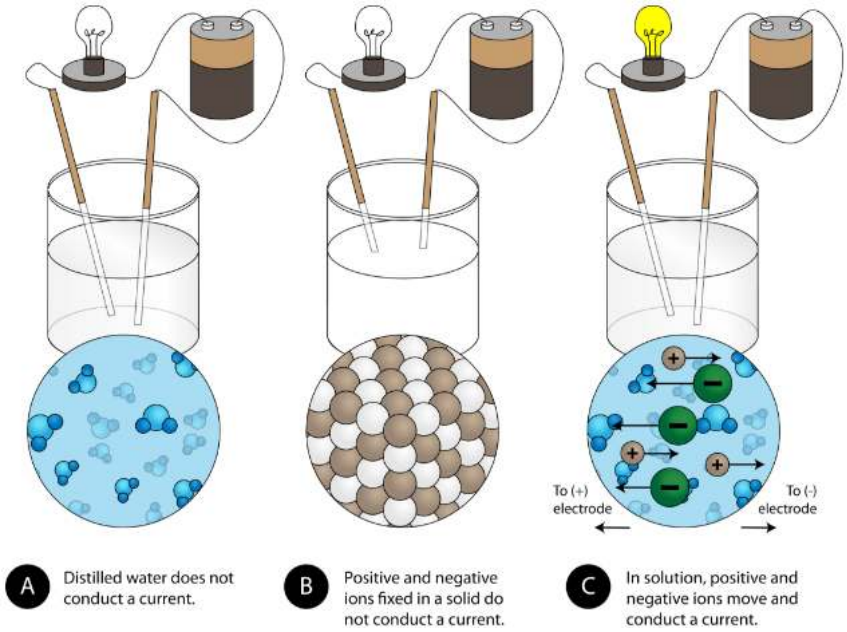



Figure 3.6.3: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

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. Cations move to one electrode, while anions move to the other, allowing electricity to flow (see figure below). Melting an ionic compound also frees the ions to conduct a current. Ionic compounds conduct an electric current when melted or dissolved in water. The dissolution of ionic compounds in water will be discussed in Section 9.3.

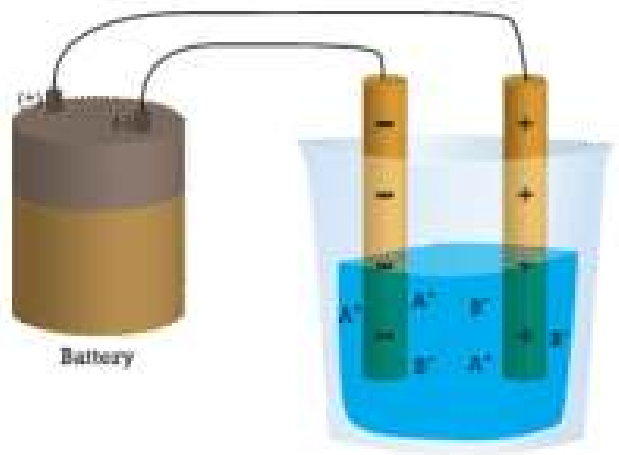



Figure 3.6.4: *In an ionic solution, the $A^+$ ions migrate toward the negative electrode, while the $B^-$ ions migrate toward the positive electrode.*


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**Example 4.7.1**

Write the dissociation equation of solid NaCl in water.

**Solution**

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

**4.7.1 Exercise**

Write the dissociation equation of solid $NH_4NO_3$ in water.

**Answer**

$NH_4NO_3(s) \rightarrow NH_4^{+}(aq) + NO_3^{-}(aq)$

## Key Takeaways

- Ionic compounds have high melting points.
- Ionic compounds are hard and brittle.
- Ionic compounds dissociate into ions when dissolved in water.
- Solutions of ionic compounds and melted ionic compounds conduct electricity, but solid materials do not.
- An ionic compound can be identified by its chemical formula: metal + nonmetal or polyatomic ions.

## Contributors and Attributions

- CK-12 Foundation by Sharon Bewick, Richard Parsons, Therese Forsythe, Shonna Robinson, and Jean Dupon.

# Exercises

1. Explain how the bonding in an ionic solid explains some of the properties of these solids.

2. Which type(s) of solid conduct(s) electricity in their liquid state but not in their solid state?

3. Based on chemical formula, identify which of the following is an ionic solid?

    a. Hg

    b. $PH_3$

    c. $Ba(NO_3)_2$

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# 4.S: Ionic Bonding and Simple Ionic Compounds (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms and ask yourself how they relate to the topics in the chapter.*

Atoms combine into compounds by forming **chemical bonds**. A survey of stable atoms and molecules leads to the **octet rule**, which says that stable atoms tend to have eight electrons in their outermost, or valence, shell. One way atoms obtain eight electrons in the valence shell is for some atoms to lose electrons while other atoms gain them. When this happens, the atoms take on an electrical charge. Charged atoms are called **ions**. Ions having opposite charges attract each other. This attraction is called **ionic bonding**, and the compounds formed are called **ionic compounds**.

Positively charged ions are called **cations**, while negatively charged ions are called **anions**. The formation of both cations and anions can be illustrated using electron configurations. Because elements in a column of the periodic table have the same valence shell electron configuration, atoms in the same column of the periodic table tend to form ions having the same charge. **Electron dot diagrams**, or **Lewis diagrams**, can also be used to illustrate the formation of cations and anions.

Ionic compounds are represented in writing by a **chemical formula**, which gives the lowest ratio of cations and anions present in the compound. In a formula, the symbol of the cation is written first, followed by the symbol of the anion. **Formula unit** is considered the basic unit of an ionic compound because ionic compounds do not exist as discrete units. Instead, they exist as **crystals**, three-dimensional arrays of ions, with cations surrounded by anions and anions surrounded by cations. Chemical formulas for ionic compounds are determined by balancing the positive charge from the cation(s) with the negative charge from the anion(s). A subscript to the right of the ion indicates that more than one of that ion is present in the chemical formula.

Some ions are groups of atoms bonded together and having an overall electrical charge. These are called **polyatomic ions**. Writing formulas with polyatomic ions follows the same rules as with monatomic ions, except that when more than one polyatomic ion is present in a chemical formula, the polyatomic ion is enclosed in parentheses and the subscript is outside the right parenthesis. Ionic compounds typically form between metals and nonmetals or between polyatomic ions.

Names of ionic compounds are derived from the names of the ions, with the name of the cation coming first, followed by the name of the anion. If an element can form cations of different charges, there are two alternate systems for indicating the compound's name. In the **Stock system**, a roman numeral in parentheses indicates the charge on the cation. An example is the name for $FeCl_2$, which is iron(II) chloride. In the common system, the suffixes *-ous* and *-ic* are used to stand for the lower and higher possible charge of the cation, respectively. These suffixes are attached to a stem representing the element (which frequently comes from the Latin form of the element name). An example is the common name for $FeCl_2$, which is ferrous chloride.

Ionic compounds are hard, brittle and have very high melting points. When in solution, the ions separate and form **electrolyte** solutions.

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# CHAPTER OVERVIEW

## 5: Covalent Bonding and Simple Molecular Compounds

Ionic bonding results from the transfer of electrons among atoms or groups of atoms. In this chapter, we will consider another type of bonding—covalent bonding. We will examine how atoms share electrons to form these bonds, and we will begin to explore how the resulting compounds, such as cholesterol, are different from ionic compounds.


5.1: Prelude to Covalent Bonding and Simple Molecular Compounds
5.2: Covalent Bonds
5.3: Covalent Compounds - Formulas and Names
5.4: Drawing Lewis Structures
5.5: Characteristics of Covalent Bonds
5.6: Characteristics of Molecules
5.7: Prelude to Solids, Liquids, and Gases
5.8: Intermolecular Interactions
5.9: Solids and Liquids
5.S: Covalent Bonding and Simple Molecular Compounds (Summary)


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# 5.1: Prelude to Covalent Bonding and Simple Molecular Compounds

Cholesterol ($C_{27}H_{46}O$), a compound that is sometimes in the news, is a white, waxy solid produced in the liver of every animal, including humans. It is important for building cell membranes and in producing certain hormones (chemicals that regulate cellular activity in the body). As such, it is necessary for life, but why is cholesterol the object of attention?

Besides producing cholesterol, we also ingest some whenever we eat meat or other animal-based food products. People who eat such products in large quantities, or whose metabolisms are unable to handle excess amounts, may experience an unhealthy buildup of cholesterol in their blood. Deposits of cholesterol, called plaque, may form on blood vessel walls, eventually blocking the arteries and preventing the delivery of oxygen to body tissues. Heart attacks, strokes, and other circulatory problems can result.

Most medical professionals recommend diets that minimize the amount of ingested cholesterol as a way of preventing heart attacks and strokes. Tests are available to measure cholesterol in the blood, and there are several drugs capable of lowering cholesterol levels.

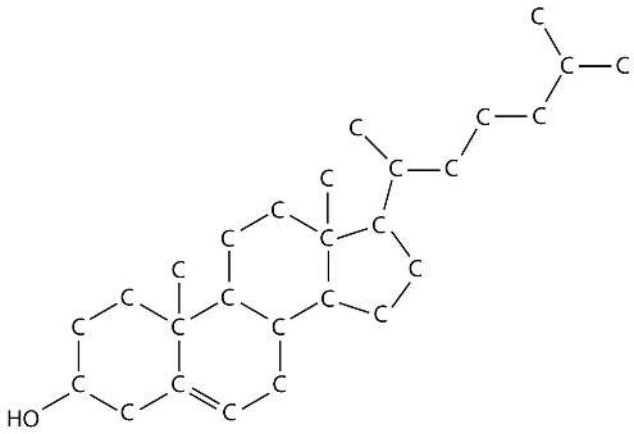



Figure 5.1.1: A Molecular Model of Cholesterol

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# 5.2: Covalent Bonds

**Learning Objectives**

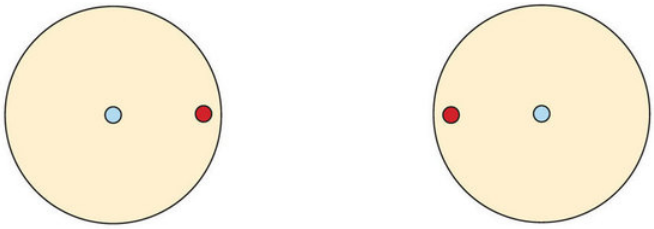
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was water ($H_2O$). You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds.

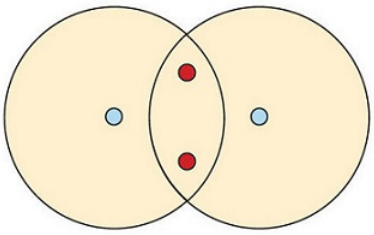
## Electron Sharing

Previously, we discussed ionic bonding where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons.

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:



In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:



By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule—the smallest part of a compound that retains the chemical identity of that compound.

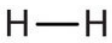
Chemists frequently use Lewis diagrams to represent covalent bonding in molecular substances. For example, the Lewis diagrams of two separate hydrogen atoms are as follows:



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



This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:



Remember that the dash, also referred to as a single bond, represents a *pair* of electrons.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about $7.4 \times 10^{-11}$ m, or 74 picometers (pm; 1 pm = $1 \times 10^{-12}$ m). This particular bond length represents 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. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

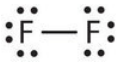
Fluorine is another element whose atoms bond together in pairs to form *diatomic* (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:



Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet** rule:



The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:



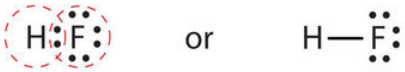
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

## Covalent Bonds between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:



Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

**Example 5.2.1**

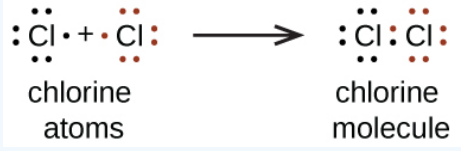
Use Lewis diagrams to indicate the formation of the following:

a. $Cl_2$
b. HBr

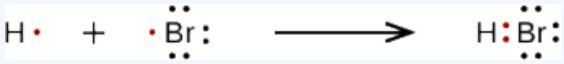
**Solution**

a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In $Cl_2$ molecule, each chlorine atom is surrounded by an **octet** number of electrons.

The Lewis diagram for a $Cl_2$ molecule is similar to the one for $F_2$ (shown above).




b. When a hydrogen atom and a bromine atom form HBr, they share one pair of electrons. In the HBr molecule, H achieves a full valence of two electrons (**duet**) while Br achieves an **octet**. The Lewis diagram for HBr is similar to that for HF shown above.



**Exercise 5.2.1**

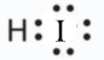
Draw the Lewis diagram for each compound.

a. a molecule composed of one chlorine atom and one fluorine atom
b. a molecule composed of one hydrogen atom and one iodine atom

**Answer a:**

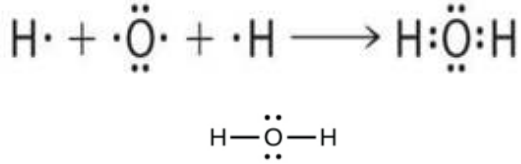


**Answer b:**



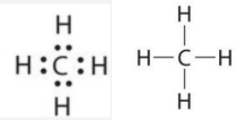
## Covalent Bonds in Larger Molecules

The formation of a water molecule from two hydrogen atoms and an oxygen atom can be illustrated using Lewis dot symbols (shown below). The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for $H_2O$. With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



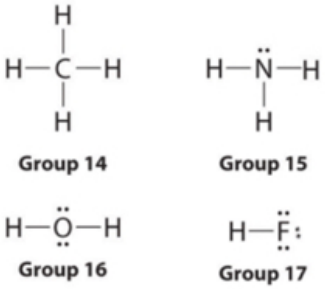
Water

Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane ($CH_4$), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis structures below. Again, sharing electrons between C and H atoms results in C achieving and octet while H achieving a duet number of electrons.



## 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). In the Lewis structure, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For example, each atom of a **group 4A** (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 $CH_4$ (methane). **Group 5A** (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 6A** (16) obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** (17) have seven valence electrons and can obtain an octet by forming **one covalent bond**.




Typically, the atoms of group 4A form 4 covalent bonds; group 5A form 3 bonds; group 6A form 2 bonds; and group 7A form one bond. 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.

| Atom (Group number) | Number of Bonds | Number of Lone Pairs |
|---|---|---|
| Carbon (Group 14 or 4A) | 4 | 0 |
| Nitrogen (Group 15 or 5A) | 3 | 1 |
| Oxygen (Group 16 or 6A) | 2 | 2 |
| Fluorine (Group 17 or 7A) | 1 | 3 |

Because hydrogen only needs two electrons to fill its valence shell, it follows the duet rule. It is an **exception to the octet rule.** Hydrogen only needs to form one bond. This is the reason why H is always a terminal atom and never a central atom. Figure **5.2.1** shows the number of covalent bonds various atoms typically form.

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.

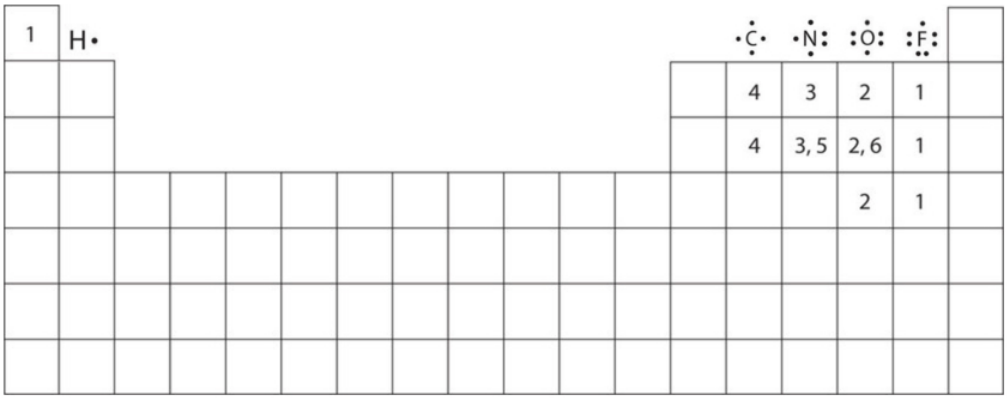
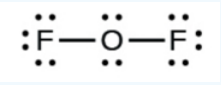



***Figure* 5.2.1*:*** *How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.*

**Example 5.2.2**

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?

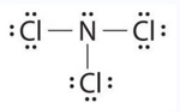


**Solution**

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 5.2.2**

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.

## 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.

## Key Takeaways

- A covalent bond is formed between two atoms by sharing electrons.
- The number of bonds an element forms in a covalent compound is determined by the number of electrons it needs to reach octet.
- Hydrogen is an exception to the octet rule. H forms only one bond because it needs only two electrons.

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# 5.3: Covalent Compounds - Formulas and Names

**Learning Objectives**

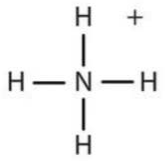
- Identify covalent and ionic compounds.
- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

## COVALENT AND IONIC COMPOUNDS

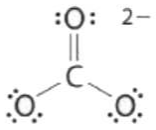
What elements make covalent bonds? Covalent bonds form when two or more nonmetals combine. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds. Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds.

As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals), silicon dioxide ($SiO_2$) will be a covalently bound molecule (a semi-metal and a non-metal) and $MgCl_2$ will be ionic (a metal and a non-metal).

A polyatomic ion is an ion composed of two or more atoms that have a charge as a group (poly = many). The ammonium ion (see figure below) consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a 1+ charge and a formula of $NH_4^+$. The carbonate ion (see figure below) consists of one carbon atom and three oxygen atoms and carries an overall charge of 2−. The formula of the carbonate ion is $CO_3^{2-}$.



ammonium ion



carbonate ion

The atoms of a polyatomic ion are tightly bonded together and so the entire ion behaves as a single unit. Several examples are found in Table 3.3.1. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride ($NH_4Cl$) has ionic bonding between a polyatomic ion, $NH_4^+$, and $Cl^-$ ions, but within the ammonium ion ($NH_4^+$), the nitrogen and hydrogen atoms are connected by covalent bonds (shown above).

Both ionic and covalent bonding are also found in calcium carbonate. Calcium carbonate ($CaCO_3$) has ionic bonding between calcium ion $Ca^{2+}$ and a polyatomic ion, $CO_3^{2-}$, but within the carbonate ion ($CO_3^{2-}$), the carbon and oxygen atoms are connected by covalent bonds (shown above).

### Characteristics of Covalent (Molecular) Compounds

Compounds that contain covalent bonds (also called molecular compounds) exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds (discussed in Section 3.6). For example, water (molecular compound) boils at 100 °C while sodium chloride (ionic compound) boils at 1413 °C. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state. The attraction between molecules (called intermolecular forces) will be discussed in more detail in Section 8.1

**Example 5.3.1**

Is each compound formed from ionic bonds, covalent bonds, or both?

a. $Na_2O$
b. $Na_3PO_4$
c. $N_2O_4$

**Answer a**

The elements in $Na_2O$ are a metal and a nonmetal, which form ionic bonds.

**Answer b**

Because sodium is a metal and we recognize the formula for the phosphate ion, we know that this compound is ionic. However, within the polyatomic phosphate ion, the atoms are held together by covalent bonds, so this compound contains both ionic and covalent bonds.

**Answer c**

The elements in $N_2O_4$| are both nonmetals, rather than a metal and a nonmetal. Therefore, the atoms form covalent bonds.

**Exercise 5.3.1**

Is each compound are formed from ionic bonds, covalent bonds, or both?

a. $Ba(OH)_2$
b. $F_2$
c. $PCl_3$

**Answer a:**

both

**Answer b:**

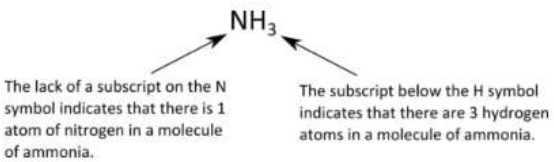
covalent

**Answer c:**

covalent

## MOLECULAR FORMULAS

The chemical formulas for covalent compounds are referred to as **molecular formulas** because these compounds exist as separate, discrete molecules. Typically, a molecular formula begins with the nonmetal that is closest to the lower left corner of the periodic table, except that hydrogen is almost never written first ($H_2O$ is the prominent exception). Then the other nonmetal symbols are listed. Numerical subscripts are used if there is more than one of a particular atom. For example, we have already seen $CH_4$, the molecular formula for methane. Below is the molecular formula of ammonia, $NH_3$.




## NAMING COVALENT COMPOUNDS

Naming *binary* (two-element) covalent compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table **5.3.1** lists these numerical prefixes. 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 **5.3.1**: 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 5.3.2**

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 5.3.2**

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 5.3.3**

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 5.3.3**

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 in Section 4.6 "Introduction to Organic Chemistry".

## Concept Review Exercises

1. How do you recognize a covalent compound?
2. What are the rules for writing the molecular formula of a simple covalent compound?
3. What are the rules for naming a simple covalent compound?

## Answers

1. A covalent compound is usually composed of two or more nonmetal elements.
2. It is just like an ionic compound except that the element further down and to the left on the periodic table is listed first and is named with the element name.
3. Name the first element first and then the second element by using the stem of the element name plus the suffix -ide. Use numerical prefixes if there is more than one atom of the first element; always use numerical prefixes for the number of atoms of the second element.

## Key Takeaways

- The chemical formula of a simple covalent compound can be determined from its name.
- The name of a simple covalent compound can be determined from its chemical formula.

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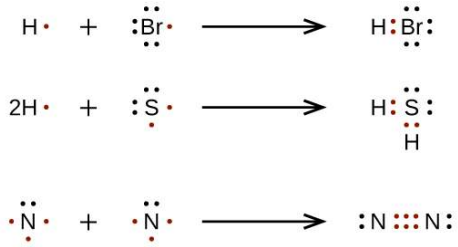
# 5.4: Drawing Lewis Structures

**Learning Objectives**

- To draw Lewis structures.
- To recognize molecules that are likely to have multiple covalent bonds.

## DRAWING LEWIS STRUCTURES

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 and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of $OF_2$ and HCN as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion. For a molecule, we add the number of valence electrons (use the main group number) on each atom in the molecule. This is the total number of electrons that must be used in the Lewis structure.

$$O + 2\,(F) = OF_2 \quad H + C + N = HCN$$

$$6e^- + (2 \times 7e^-) = 20e^- \quad 1e^- + 4e^- + 5e^- = 10e^-$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. Note that H and F can only form one bond, and are always on the periphery rather than the central atom.



3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

- In $OF_2$, six electrons are placed on each F.
- In HCN, six electrons placed on N



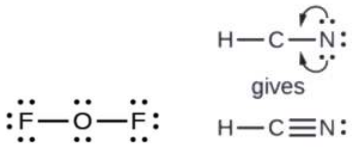
4. Place all remaining electrons on the central atom.

- In $OF_2$, 4 electrons are placed on O.
- In HCN: no electrons remain (the total valence of $10e^-$ is reached) so nothing changes.



5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

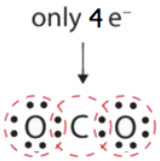
- In $OF_2$, each atom has an octet as drawn, so nothing changes.
- In HCN, form two more C–N bonds




Finally, check to see if the total number of valence electrons are present in the Lewis structure. And then, inspect if the H atom has 2 electrons surrounding it and if each of the main group atoms is surrounded by 8 electrons.

## MULTIPLE BONDS

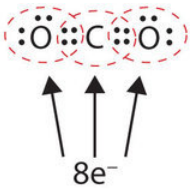
In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares only two electrons. Review HCN in Step 5 above. Another example is carbon dioxide ($CO_2$). $CO_2$ has a total valence of $4e^- + (2 \times 6e^-) = 16e^-$. Following steps 1 to 4, we draw the following:



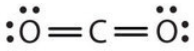

This does not give the carbon atom a complete octet; only four electrons are in its valence shell. This arrangement of shared electrons is far from satisfactory.



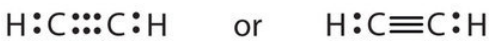
In this case, more than one pair of electrons must be shared between two atoms for both atoms to have an octet. A second electron pair from each oxygen atom must be shared with the central carbon atom shown by the arrows above. A lone pair from each O must be converted into a bonding pair of electrons.




In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a double bond between the atoms, which is represented by a double dash:



Some molecules contain triple bonds (like HCN, shown above). Triple bonds are covalent bonds in which *three* pairs of electrons are shared by two atoms. Another compound that has a triple bond is acetylene ($C_2H_2$), whose Lewis diagram is as follows:



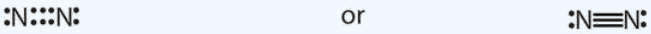
## Example 5.4.1

Draw the Lewis diagram for each molecule.

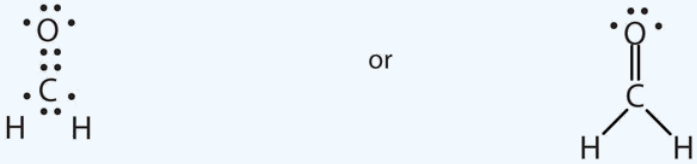
1. **$N_2$**
2. **$CH_2O$** (The carbon atom is the central atom.) One application of $CH_2O$, also called formaldehyde, is the preservation of biological specimens. Aqueous solutions of $CH_2O$ are called formalin and have a sharp, characteristic (pungent) odor.

**Solution**

1. The total number of electrons is 2 x 5 = 10 electrons. The bond between the two nitrogen atoms is a triple bond. The Lewis diagram for $N_2$is as follows:



2. The total number of electrons is 4 x 2(1) + 6 = 12 electrons. In $CH_2O$, the central atom is surrounded by two different types of atoms. The Lewis diagram that fills each atom's valence electron shell is as follows:

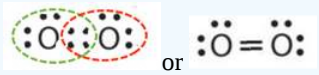


## Exercise 5.4.1

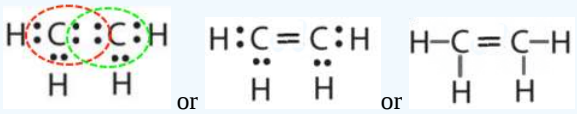
Draw the Lewis diagram for each molecule.

a. **$O_2$**
b. **$C_2H_4$**

**Answer a:**

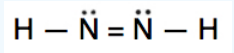


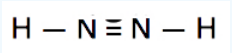
**Answer b:**

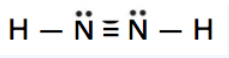


## Example 5.4.2

Which is the correct Lewis structure for $N_2H_2$?

A. 

B. 

C. 

**Solution**

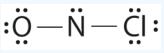
Lewis structure A is the correct answer. It has a total of (2 x $5e^-$) + (2 x $1e^-$) = $12e^-$. Each of the N atoms satisfy the octet requirement and the H atoms follow the duet rule.

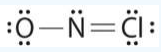
Structure B is electron deficient. It has only $10e^-$ instead of 12.

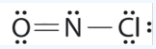
Structure C has 14 (2 extra) electrons. The N atoms do not satisfy the octet.

**Exercise 5.4.2**

Which is the correct Lewis structure for NOCl?

A. 

B. 

C. 

**Answer**

Structure A violates the octet rule; N is surrounded by only $6e^-$.

Structure B violates the octet rule; Cl has $10e^-$ around it. Furthermore, there are a total of $20e^-$ instead of $18e^-$.

Structure C is the correct structure. It has a total of $6e^-$ + $5e^-$ + $7e^-$ = $18e^-$. Each atom is surrounded by 8 electrons (octet rule).

## Key Takeaways

- A Lewis structure shows the bonding and nonbonding electrons around individual atoms in a molecule.
- Some molecules must have multiple covalent bonds between atoms to satisfy the octet rule.
- A double bond contains four electrons and a triple bond contains six electrons.

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# 5.5: Characteristics of Covalent Bonds

**Learning Objectives**

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

## Bond Length

We previously stated that the covalent bond in the hydrogen molecule ($H_2$) has a certain length (about $7.4 \times 10^{-11}$ m). Other covalent bonds also have known bond lengths, which are dependent on both the identities of the atoms in the bond and whether the bonds are single, double, or triple bonds. Table **5.5.1** lists the approximate bond lengths for some single covalent bonds. The exact bond length may vary depending on the identity of the molecule but will be close to the value given in the table.

Table **5.5.1**: Approximate Bond Lengths of Some Single Bonds

| Bond | Length ($\times 10^{-12}\,m$) |
|---|---|
| H–H | 74 |
| H–C | 110 |
| H–N | 100 |
| H–O | 97 |
| H–I | 161 |
| C–C | 154 |
| C–N | 147 |
| C–O | 143 |
| N–N | 145 |
| O–O | 145 |

Table **5.5.2** compares the lengths of single covalent bonds with those of double and triple bonds between the same atoms. Without exception, as the number of covalent bonds between two atoms increases, the bond length decreases. With more electrons between the two nuclei, the nuclei can get closer together before the internuclear repulsion is strong enough to balance the attraction.

Table **5.5.2**: Comparison of Bond Lengths for Single and Multiple Bonds

| Bond | Length ($\times 10^{-12}\,m$) |
|---|---|
| C–C | 154 |
| C=C | 134 |
| C≡C | 120 |
| C–N | 147 |
| C=N | 128 |
| C≡N | 116 |
| C–O | 143 |
| C=O | 120 |
| C≡O | 113 |
| N–N | 145 |
| N=N | 123 |
| N≡N | 110 |
| O–O | 145 |
| O=O | 121 |

## Electronegativity and Bond Polarity

Although we defined covalent bonding as electron sharing, the electrons in a covalent bond are not always shared equally by the two bonded atoms. Unless the bond connects two atoms of the same element, as in $H_2$, there will always be one atom that attracts the electrons in the bond more strongly than the other atom does, as in HCl, shown in Figure 5.5.1. A covalent bond that has an equal sharing of electrons (Figure 5.5.1*a*) is called a **nonpolar covalent bond**. A covalent bond that has an unequal sharing of electrons, as in Figure 5.5.1*b*, is called a **polar covalent bond**.

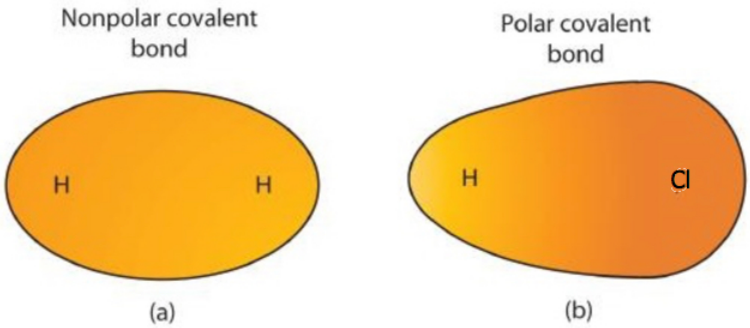



Figure 5.5.1 Polar versus Nonpolar Covalent Bonds. (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The chlorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. This is a polar covalent bond.

The distribution of electron density in a polar bond is uneven. It 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 5.5.1*b* 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). This is seen in Figure 5.5.2*a*. The separation of

charge in a polar covalent bond results in an electric dipole (two poles), represented by the arrow in Figure 5.5.2b. The direction of the arrow is pointed toward the δ− end while the + tail of the arrow indicates the δ+ end of the bond.

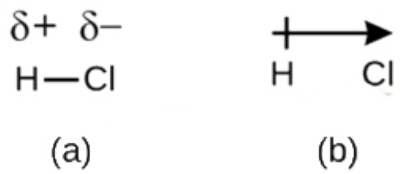



Figure 5.5.2: (a) Unequal sharing of the bonding pair of electrons between H and Cl leads to partial positive charge on the H atom and partial negative charge on the Cl. Symbols δ+ and δ– indicate the polarity of the H–Cl bond. (b) The dipole is represented by an arrow with a cross at the tail. The cross is near the δ+ end and the arrowhead coincides with the δ–.

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. There are various numerical scales for rating electronegativity. Figure 5.5.3 shows one of the most popular—the Pauling scale.

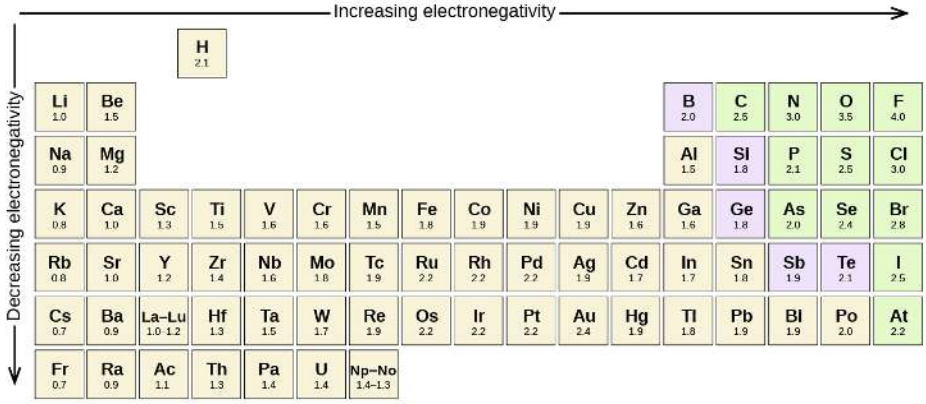
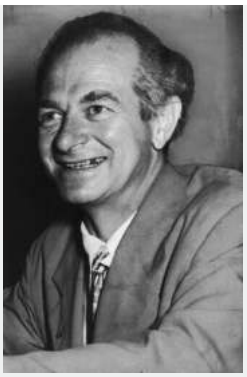



Figure 5.5.3 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).

## 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.

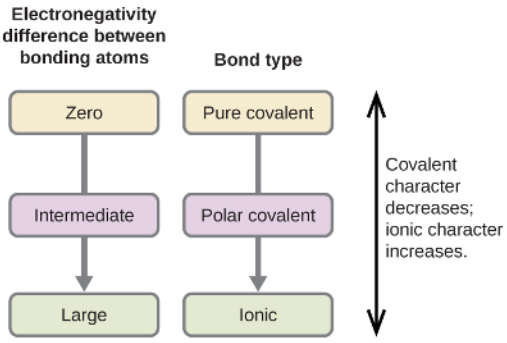
By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.)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

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 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.**




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

Figure **5.5.4**: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

**Polar Bonds Video**

**Example 5.5.1**

Determine if the bonds between the atoms below are ionic, nonpolar covalent or polar covalent.

a. F - H
b. H - H
c. Na - Cl
d. O - H

**Solution**

a. Polar covalent bond.
b. Nonpolar covalent bond.
c. Ionic bond.
d. Polar covalent bond.

**Exercise 5.5.1**

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:**

Polar covalent bond. The sharing of electrons between C and O is unequal with the electrons more strongly drawn towards O.

**Answer b:**

Ionic bond.

**Answer c:**

Identical atoms have zero EN difference, hence nonpolar covalent bond.

**Answer d:**

Ionic bond.

## Bond Polarity and Molecular 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**. A **polar molecule** *is a molecule in which 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 is called a* **dipole**. A simplified way to depict polar molecules like HF is pictured below (see figure below).

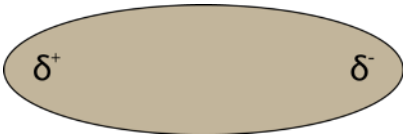



Figure 5.5.5: A molecular dipole results from the unequal distribution of electron density throughout a molecule.

When placed between oppositely charged plates, polar molecules orient themselves so that their positive ends are closer to the negative plate and their negative ends are closer to the positive plate (see Figure 4.4.6 below).

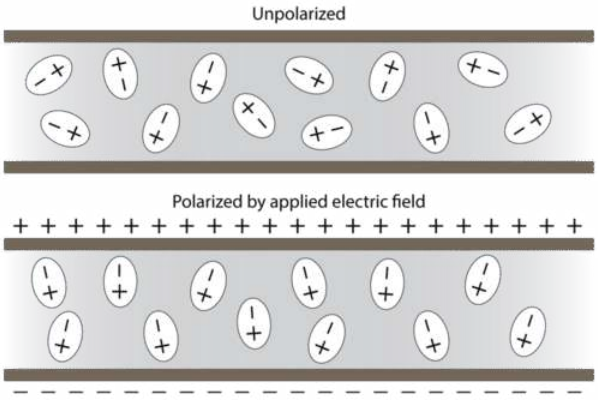



Figure 5.5.6: Polar molecules are randomly oriented in the absence of an applied electric field (top). In an electric field, the molecules orient themselves to maximize the attraction between opposite charges (bottom).

Experimental techniques involving electric fields can be used to determine if a certain substance is composed of polar molecules and to measure the degree of polarity.

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. (Figure **5.5.7**) is a comparison between carbon dioxide and water. Carbon dioxide ($CO_2$) is a **linear** molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented directly opposite each other, they cancel each other out, and the overall molecular polarity of $CO_2$ is zero. $CO_2$ is a **nonpolar** molecule. In $H_2O$, the orientation of the two O–H bonds is **bent**: one end of the molecule has a partial positive charge, and the other end has a partial negative charge. In short, the molecule itself is **polar**. The polarity of water has an enormous impact on its physical and chemical properties. For example, the boiling point of water (100°C) is high for such a small molecule due to the fact that polar molecules attract each other strongly. On the other hand, the nonpolar carbon dioxide becomes a gas at −77°C, almost 200° lower than the temperature at which water boils. More details will be presented in the next section.




Figure **5.5.7** Physical Properties and Polarity. The physical properties of water and carbon dioxide are affected by their polarities.

## Concept Review Exercises

1. What is the name for the distance between two atoms in a covalent bond?
2. What does the electronegativity of an atom indicate?
3. What type of bond is formed between two atoms if the difference in electronegativities is small? Medium? Large?

## Answers

1. bond length
2. Electronegativity is a qualitative measure of how much an atom attracts electrons in a covalent bond.
3. nonpolar; polar; ionic

## Key Takeaways

- Covalent bonds between different atoms have different bond lengths.
- Covalent bonds can be polar or nonpolar, depending on the electronegativity difference between the atoms involved.

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# 5.6: Characteristics of Molecules

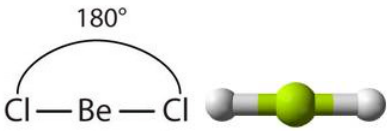
**Learning Objectives**

- Predict the general shape of a simple covalent molecule.
- Predict the polarity of the molecule.
- Compare the properties of ionic and molecular compounds.

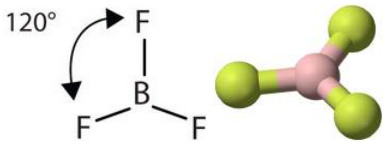
Unlike the ions in ionic compounds, which are arranged in lattices called crystals, molecules of covalent compounds exist as discrete units with a characteristic mass and a certain three-dimensional shape.

## Molecular Shape: VSEPR Theory

Unlike ionic compounds, with their extended crystal lattices, covalent molecules are discrete units with specific three-dimensional shapes. The shape of a molecule is determined by the fact that covalent bonds, which are composed of negatively charged electrons, tend to repel one another. This concept is called the **valence shell electron pair repulsion (VSEPR) theory**. For example, the two covalent bonds in $\mathbf{BeCl_2}$ **stay as far from each other** as possible, ending up 180° apart from each other. The result is a ***linear*** molecule:



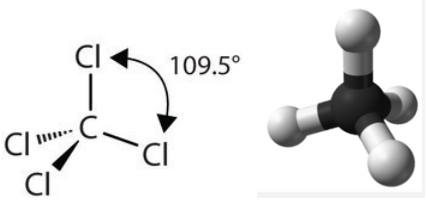

The three covalent bonds in $BF_3$ repel each other to form 120° angles in a plane, in a shape called ***trigonal planar***:




The molecules $\mathbf{BeCl_2}$ and $\mathbf{BF_3}$ actually violate the octet rule; however, such exceptions are rare and will not be discussed in this text.

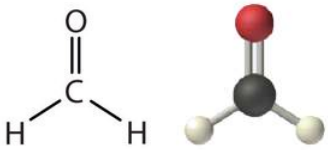
> Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your “bonds” are farther apart than the planar 120° orientation.

The four covalent bonds in $CCl_4$ arrange themselves three dimensionally, pointing toward the corner of a tetrahedron and making bond angles of 109.5°. $CCl_4$ is said to have a ***tetrahedral*** shape:



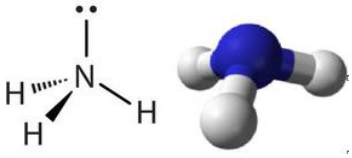

| Atoms Around Central Atom | Geometry | Example |
|---|---|---|
| 2 $\mathbf{AB_2}$ | Linear | $\mathbf{BeCl_2}$ |
| 3 $\mathbf{AB_3}$ | Trigonal Planar | $\mathbf{BF_3}$ |
| 4 $\mathbf{AB_4}$ | Tetrahedral | $\mathbf{CCl_4}$ |

In determining the shapes of molecules, it is useful to first determine the Lewis diagram for a molecule. The shapes of molecules with multiple bonds are determined by treating the multiple bonds as one bond. Thus, formaldehyde ($CH_2O$) has a shape similar to that of $BF_3$. It is ***trigonal planar***.

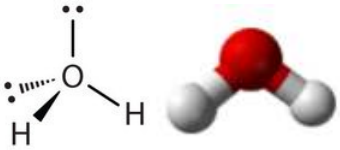



## Molecules With Lone Pairs Around Central Atom

Molecules with lone electron pairs around the central atom have a shape based on the position of the atoms, not the electron pairs. For example, $NH_3$ has **one lone electron pair** and **three bonded electron pairs**. These four electron pairs repel each other and adopt a tetrahedral arrangement. However, the shape of the molecule is described in terms of the positions of the atoms, not the lone electron pairs. Thus, $NH_3$ is said to have a ***trigonal pyramidal*** shape, not a tetrahedral one.




Similarly, $H_2O$ has **two lone pairs** of electrons around the central oxygen atom and **two bonded electron pairs**. Although the four electron pairs adopt a tetrahedral arrangement, the shape of the molecule is described by the positions of the atoms only. The shape of $H_2O$ is ***bent*** with an approximate 109.5° angle.




In summary, to determine the molecular geometry:

Step 1: Draw the Lewis structure.

Step 2: Count the number of bonds (a double/triple bond counts as one) and lone pairs around the **central atom**.

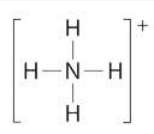
Step 3: Use Table 4.5.1 to determine the molecular geometry.

| Number of bonds and lone pairs | Number of bonds<br>0 lone pair | 1 lone pair | 2 lone pairs |
|---|---|---|---|
| 2 | 180°<br>X–A–X<br>Linear | | |
| 3 | 120°<br>Trigonal planar | <120°<br>Bent or angular | Lone Pair |
| 4 | 109°<br>Tetrahedral | <109°<br>Trigonal pyramid | <<109°<br>Bent or angular |

*Table 4.5.1: The molecular geometry depends on the number of bonds and lone pairs around the* **central atom, A.**

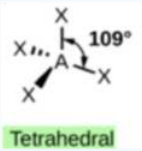
**Example 5.6.1**

What is the geometry of the ammonium ion, $NH_4^+$? Its Lewis structure is shown below. How is this different from ammonia, $NH_3$?

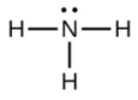


**Solution**

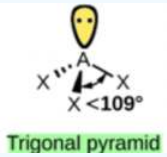
In ammonium ion, the central atom N has 4 bonds and no lone pair. It is equivalent to the below in Table 4.5.1. Hence, this is *tetrahedral*.




In ammonia ($NH_3$), shown below, N has 3 bonds and one lone pair.

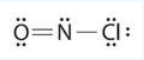


It is equivalent to the below in Table 4.5.1. Hence, the shape of this molecule is *trigonal pyramid*.



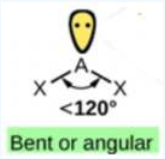

**Exercise 5.6.1**

What is the molecular shape of nitrosyl chloride, a highly corrosive, reddish-orange gas? Its Lewis structure is shown below.



**Answer**

Focus on the central atom, N. It has a double bond to O, count this as one bond. It also has a single bond to Cl. Thus, N has 2 bonds and one lone pair. These 3 electron pairs will spread out 120 degrees from each other. But, since the shape is defined by the arrangement of the atoms only, the shape is bent or angular. If you consult Table 4.5.1, this molecule is equivalent to the below. Hence, two bonds and one lone pair has a *bent or angular* shape.



## Molecular Polarity

In general, a molecule is nonpolar if all its bonds are nonpolar. Examples are $I_2$, $O_2$, $H_2$, $CH_4$, $C_2H_6$ and $C_3H_8$.

In general, a molecule is polar if it contains polar bonds EXCEPT when the bond polarities cancel each other. As mentioned in Section 4.4, the shape of the $CO_2$ molecule (linear) orients the two C=O polar bonds **directly opposite** each other, thus **cancelling** each other's effect. **Carbon dioxide** ($CO_2$) is a ***nonpolar*** molecule.

On the other hand, water (as discussed above) is a bent molecule because of the two lone pairs on the central oxygen atom. Because of the bent shape, the dipoles do not cancel each other out and the water molecule is ***polar***. In the figure below, the individual H-O polar bonds represented by the two red arrows are not directly opposite each other. These two dipoles don't cancel each other out. In fact, the net dipole (blue arrow) points upward. There is a resultant partial positive charge at one end (between the two H atoms) and a partial negative charge on the other end (where O is located). The uneven distribution of charge or the overall dipole is shown by the blue arrow below (Figure 4.5.1). Hence, **water is *polar*** (has + and - poles) while **carbon dioxide is *nonpolar***.

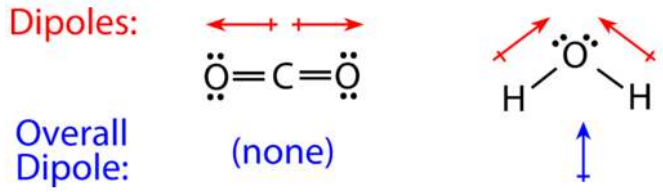



Figure 4.5.1: *The molecular geometry of a molecule (linear vs. bent) affects its polarity.*

Similarly, in $BF_3$ (trigonal planar), the effect of a B-F bond is cancelled by the sum of the other two B-F bonds (see video). Hence, a trigonal planar molecule ($BF_3$) is nonpolar because the bond polarities cancel each other, but a trigonal pyramidal molecule ($NH_3$) is polar.

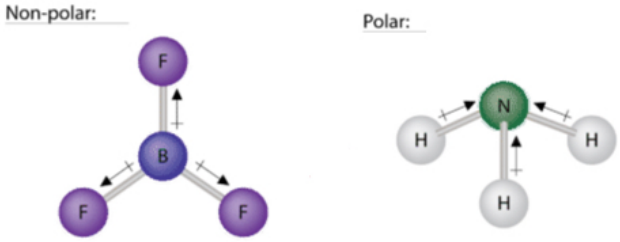



Figure 4.5.2: *The molecular geometry of a molecule (trigonal planar vs. trigonal pyramid) affects its polarity.*

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as $CCl_4$ is ***nonpolar***. However, if the peripheral atoms are not of the same electronegativity, the bond polarities don't cancel and the molecule becomes ***polar***, as in $CH_3Cl$.

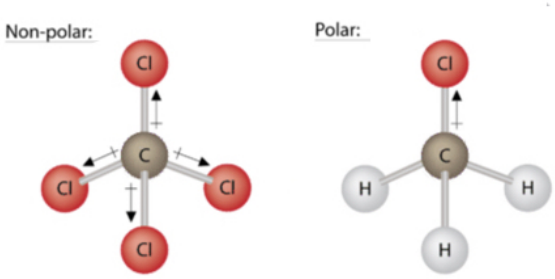



Figure 4.5.3: *The same molecular geometry but peripheral bonds are of different electronegativity. $CCl_4$ is nonpolar but $CH_3Cl$ is polar.*

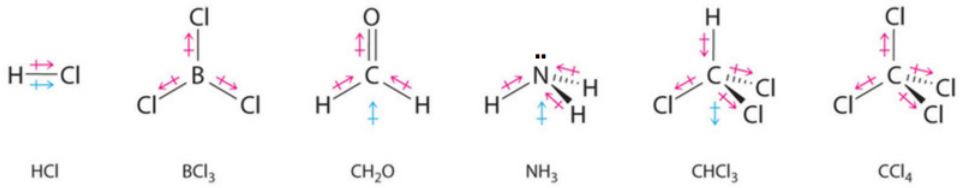



Figure **5.6.4**: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional geometry, some molecules with polar bonds have a net dipole moment (HCl, $CH_2O$, $NH_3$, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipoles cancel due to symmetry ($BCl_3$ and $CCl_4$).

## Physical Properties of 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 in Section 8.1) 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.

| **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 |

**Table 4.5.2: Comparison of Ionic and Molecular Compounds**

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.

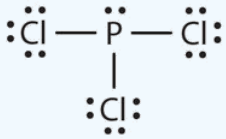
**Example 5.6.2**

Describe the shape of each molecule. Is it polar or nonpolar?

a. $PCl_3$
b. $CO_2$

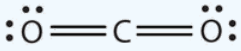
**Solution**

a. The Lewis diagram for $PCl_3$ is as follows:



Focus on the central atom, P that has 3 bonds and one lone pair. The four electron pairs arrange themselves tetrahedrally, but the lone electron pair is not considered in describing the molecular shape. Like $NH_3$, this molecule is *pyramidal*. The 3 P-Cl bonds don't cancel each other. This is *polar.*

b. The Lewis diagram for $CO_2$ is as follows:



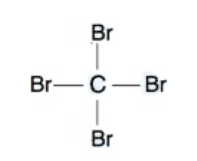
Focus on the central atom, C. The multiple bonds are treated as one group, hence C has 2 bonds and zero lone pair. $CO_2$ has only two groups of electrons that repel each other. They will direct themselves 180° apart from each other, so $CO_2$ molecules are *linear*. This is highly symmetrical, with the two opposite dipoles cancelling each other. The $CO_2$ molecule is *nonpolar*.

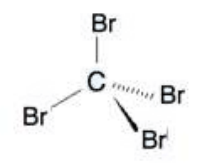
## Exercise 5.6.2

Describe the shape of each molecule. Is it polar or nonpolar?

a. $CBr_4$
b. $BCl_3$

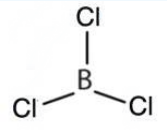
**Answer a:**



or



The Lewis structure shows 4 groups attached to the central atom, hence *tetrahedral*. All the 4 groups are identical and the shape is symmetrical. Hence, it is *nonpolar.*

**Answer b:**




The Lewis diagram shows 3 groups attached to the central atom, hence *trigonal planar*. All the 3 groups are identical and shape is symmetrical, hence, it is *nonpolar.*

## Concept Review Exercises

1. How do you determine the shape of a molecule?
2. How do you determine whether a molecule is polar or nonpolar?

## Answers

1. The shape of a molecule is determined by the position of the atoms, which in turn is determined by the repulsion of the bonded and lone electron pairs around the central atom.
2. If all the bonds in a molecule are nonpolar, the molecule is nonpolar. If it contains identical polar bonds that are oriented symmetrically opposite each other (linear, trigonal planar or tetrahedral) then the molecule is nonpolar. If it contains polar bonds that don't cancel each other's effects, the molecule is polar.

## Key Takeaways

- Simple molecules have geometries that can be determined from VSEPR theory.
- Polar molecules result from differences in electronegativity of the atoms in the molecule.
- Dipoles that are directly opposite one another cancel each other out.

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# 5.7: Prelude to Solids, Liquids, and Gases

We normally experience carbon dioxide ($CO_2$) as a gas, but if it were cooled down to about −78°C, it would become a solid. The everyday term for solid carbon dioxide is dry ice.

Why “dry” ice? Solid carbon dioxide is called dry ice because it converts from a solid to a gas directly, without going through the liquid phase, in a process called sublimation. Thus, there is no messy liquid phase to worry about. Although it is a novelty, dry ice has some potential dangers. Because it is so cold, it can freeze living tissues very quickly, so people handling dry ice should wear special protective gloves. The cold carbon dioxide gas is also heavier than air (because it is cold and more dense), so people in the presence of dry ice should be in a well-ventilated area.



Figure **5.7.1**: Dry ice. (CC BY SA 3.0 unported; ProjectManhattan).

Dry ice has several common uses. Because it is so cold, it is used as a refrigerant to keep other things cold or frozen (e.g., meats or ice cream). In the medical field, dry ice is used to preserve medical specimens, blood products, and drugs. It also has dermatological applications (e.g., freezing off warts). Organs for transplant are kept cool with dry ice until the recipient of the new organ is ready for surgery. In this respect, carbon dioxide is much like water—more than one phase of the same substance has significant uses in the real world.

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# 5.8: Intermolecular Interactions

**Learning Objectives**

- Define *phase*.
- Identify the types of interactions between molecules.

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). Not all substances will readily exhibit all phases. For example, carbon dioxide does not exhibit a liquid phase unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose at higher temperatures, rather than becoming a liquid or a gas.

> *For many substances, there are different arrangements the particles can take in the solid phase, depending on temperature and pressure.*

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, $H_2O$ exists in the solid form as ice. When it is warmer, the liquid phase of $H_2O$ is present. At even higher temperatures, $H_2O$ boils and becomes steam.

Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases, mentioning pressure effects only when they are important. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather extreme. Table 5.8.1 shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges.

Table 5.8.1: Temperature Ranges for the Three Phases of Various Substances

| Substance | Solid Phase Below | Liquid Phase Above | Gas Phase Above |
|---|---|---|---|
| hydrogen ($H_2$) | −259°C | −259°C | −253°C |
| water ($H_2O$) | 0°C | 0°C | 100°C |
| sodium chloride (NaCl) | 801°C | 801°C | 1413°C |

The *melting point* of a substance is the temperature that separates a solid and a liquid. The *boiling point* of a substance is the temperature that separates a liquid and a gas.

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the **intermolecular forces (IMF)** between the **particles** of substances and the **kinetic energies** (KE) of its molecules. (Although ionic compounds are not composed of discrete molecules, we will still use the term *intermolecular* to include interactions between the ions in such compounds.) Substances that experience **strong intermolecular interactions** require **higher temperatures to become liquids and, finally, gases.** Substances that experience **weak intermolecular interactions** do not need much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at **lower temperatures.**

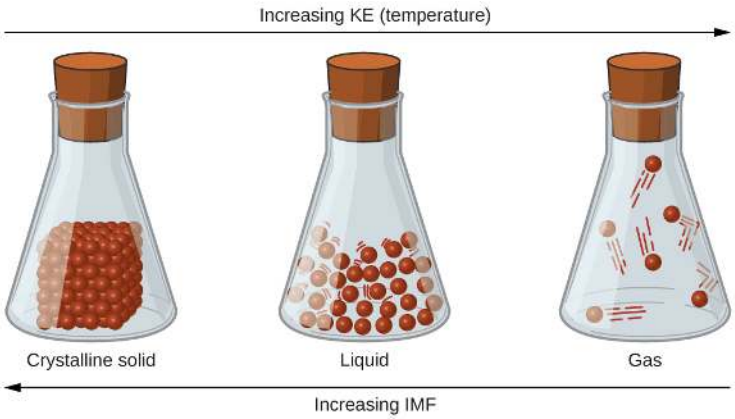



Figure 5.8.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

## Covalent Network Materials

Substances with the highest melting and boiling points have **covalent network** bonding. This type of intermolecular interaction is actually a covalent bond. In these substances, all the atoms in a sample are covalently bonded to one another; in effect, the entire sample is essentially **one giant molecule**. Many of these substances are solid over a large temperature range because it takes a lot of energy to disrupt all the covalent bonds at once. One example of a substance that shows covalent network bonding is diamond (Figure 5.8.2). Diamond is composed entirely of carbon atoms, each bonded to four other carbon atoms in a tetrahedral geometry. Melting a covalent network solid is not accomplished by overcoming the relatively weak intermolecular forces. Rather, all of the covalent bonds must be broken, a process that requires extremely high temperatures. Diamond, in fact, does not melt at all. Instead, it vaporizes to a gas at temperatures above 3,500°C. Diamond is extremely hard and is one of the few materials that can cut glass.

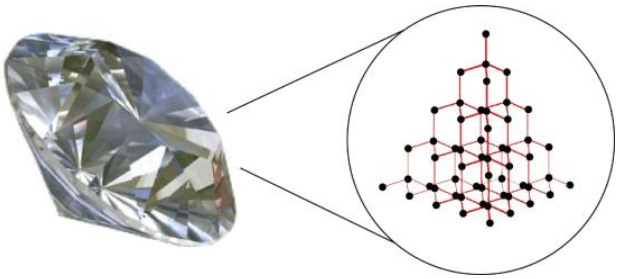


Figure 5.8.2: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state. Source: Photo © Thinkstock

## Ionic Compounds

The strongest force between any two particles is the ionic bond, in which two ions of opposing charge are attracted to each other. Thus, ionic interactions between particles are another type of intermolecular interaction. Substances that contain ionic interactions are relatively strongly held together, so these substances typically have high melting and boiling points. Sodium chloride (Figure 5.8.3) is an example of a substance whose particles experience ionic interactions (Table 5.8.1). These attractive forces are sometimes referred to as ion-ion interactions.

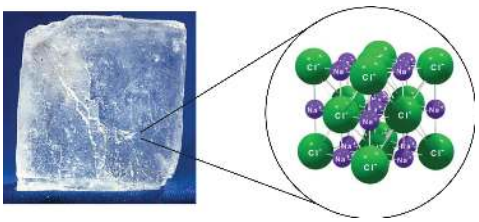


Figure 5.8.3: Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock

## Covalent Molecular Compounds

There are two different covalent structures: molecular and network. Covalent network compounds like $SiO_2$ (quartz) have structures of atoms in a network like diamond described earlier. In this section, we are dealing with the molecular type that contains individual molecules. The bonding between atoms in the individual molecule is covalent but the attractive forces between the molecules are called ***intermolecular forces (IMF)***.

In contrast to *intramolecular* forces (see Figure 8.1.4), such as the covalent bonds that hold atoms together in molecules and polyatomic ions, intermolecular forces hold molecules together in a **liquid or solid**. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances ***without breaking covalent bonds*.**

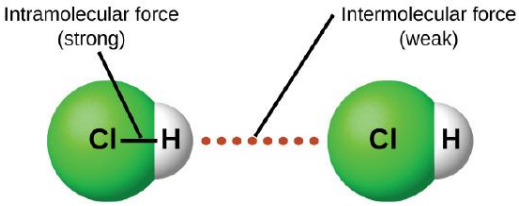



Figure **5.8.4**: **Intramolecular** forces keep a molecule intact. **Intermolecular** forces hold multiple molecules together and determine many of a substance's properties.

In this section, we will discuss the three types of IMF in molecular compounds: dipole-dipole, hydrogen bonding and London dispersion forces.

## Dipole-dipole Intermolecular Forces

As discussed in Section 4.4, covalent bond that has an unequal sharing of electrons is called a **polar covalent** bond. (A covalent bond that has an equal sharing of electrons, as in a covalent bond with the same atom on each side, is called a **nonpolar covalent** bond.) A molecule with a net unequal distribution of electrons in its covalent bonds is a polar molecule. HF is an example of a polar molecule (see Figure 8.1.5).




Figure **5.8.5**: Polar Covalent Bonds. The electrons in the HF molecule are not equally shared by the two atoms in the bond. Because the fluorine atom has nine protons in its nucleus, it attracts the negatively charged electrons in the bond more than the hydrogen atom does with its one proton in its nucleus. Thus, electrons are more strongly attracted to the fluorine atom, leading to an imbalance in the electron distribution between the atoms. The fluorine side of the bond picks up a partial overall negative charge (represented by the δ− in the diagram), while the hydrogen side of the bond has an overall partial positive charge (represented by the δ+ in the diagram). Such a bond is called a *polar covalent bond*.

The charge separation in a **polar covalent bond** is not as extreme as is found in ionic compounds, but there is a related result: oppositely charged ends of different molecules will attract each other. This type of intermolecular interaction is called a **dipole-dipole interaction**. Many molecules with polar covalent bonds experience dipole-dipole interactions.

The covalent bonds in some molecules are oriented in space in such a way that the bonds in the molecules cancel each other out. The individual bonds are polar, but due to molecular symmetry, the overall molecule is not polar; rather, the molecule is ***nonpolar*.** Such molecules experience little or no dipole-dipole interactions. Carbon dioxide ($CO_2$) and carbon tetrachloride ($CCl_4$) are examples of such molecules (Figure **5.8.6**).

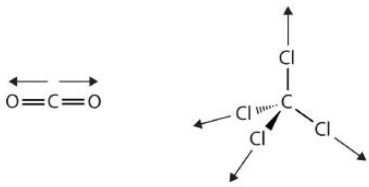



Figure 5.8.6: Nonpolar Molecules. Although the individual bonds in both $CO_2$ and $CCl_4$ are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

Recall from the Sections 4.4 and 4.5, on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole.*** Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 5.8.7.

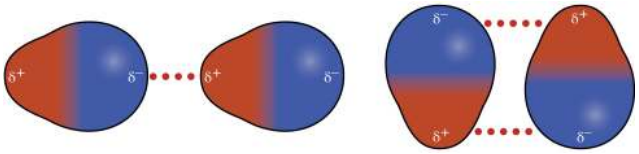



Figure 5.8.7: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar $F_2$ molecules. Both HCl and $F_2$ consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average kinetic energy. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar $F_2$ molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to $F_2$ (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar $F_2$ molecules. We will often use values such as boiling or freezing points as indicators of the relative strengths of IMFs of attraction present within different substances.

**Example 5.8.1**

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 5.8.1**

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 Bonding Intermolecular Forces

Molecules with **hydrogen atoms** bonded to electronegative atoms such as **O, N, and F** tend to exhibit unusually strong intermolecular interactions due to a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to ***highly concentrated partial charges*** with these atoms. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs of electrons.

Examples of hydrogen bonds include HF···HF, $H_2O$···HOH, and $H_3N$···$HNH_2$, in which the **hydrogen bonds** are denoted by **dots**. Figure 5.8.8 illustrates hydrogen bonding between water molecules. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding between water molecules. Most molecular compounds that have a mass similar to water are gases at room temperature. However, because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state.

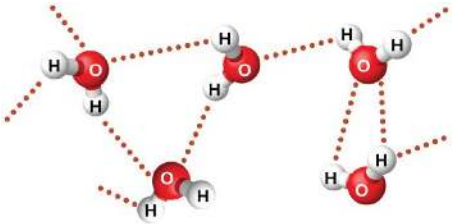


Figure 5.8.8: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

A **hydrogen bond** is an intermolecular attractive force in which *a* **hydrogen atom**, that is covalently bonded to a small, highly electronegative atom, is attracted to a **lone pair of electrons** on an atom in a neighboring molecule. Figure 5.8.9 shows how methanol ($CH_3OH$) molecules experience hydrogen bonding. Methanol contains both a hydrogen atom attached to O; methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor (lone pair). The hydrogen-bonded structure of methanol is as follows:

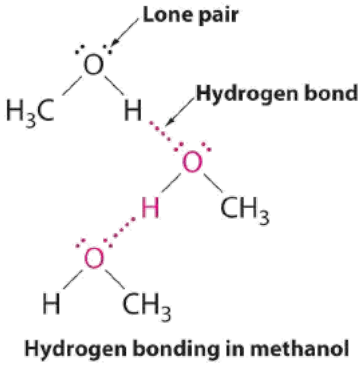



Figure 5.8.9: Methanol molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

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.

### Effect of Hydrogen Bonding on Boiling Points

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 5.8.2**

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.

## 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 5.8.10.

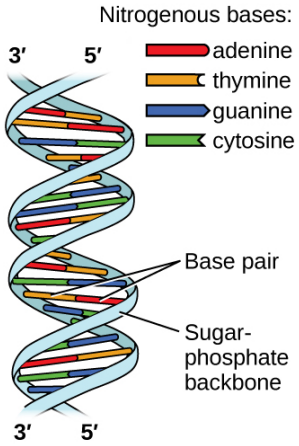



Figure 5.8.10: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

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 5.8.11

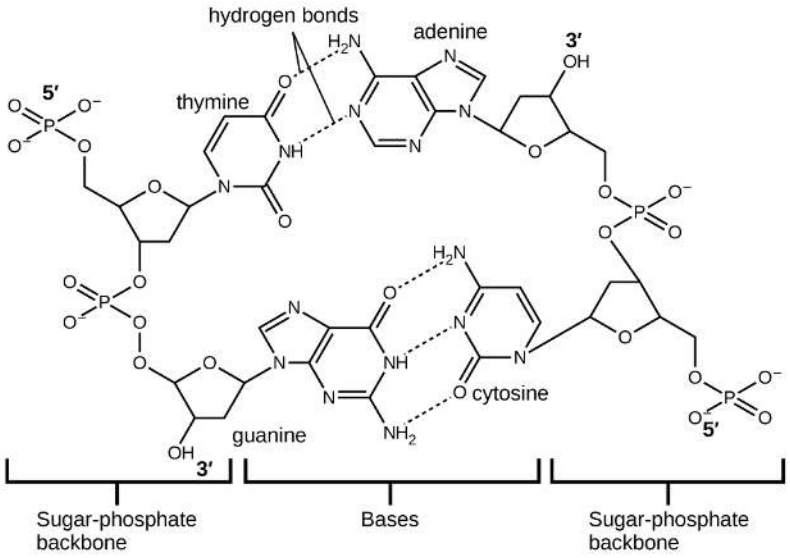



Figure 5.8.11: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

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.

## London Dispersion Forces

Finally, 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 that disappears almost as soon as it appears. These are very weak intermolecular interactions and are called **dispersion forces (or London forces)**. (An alternate name is London dispersion forces.) Molecules that experience no other type of intermolecular interaction will at least experience dispersion forces. Substances that experience only dispersion forces are typically soft in the solid phase and have relatively low melting points. Examples include *waxes*, which are long hydrocarbon chains that are solids at room temperature because the molecules have so many electrons. The resulting dispersion forces between these molecules make them assume the solid phase at normal temperatures.

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 8.1.2.

Table 5.8.2: **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 5.8.3

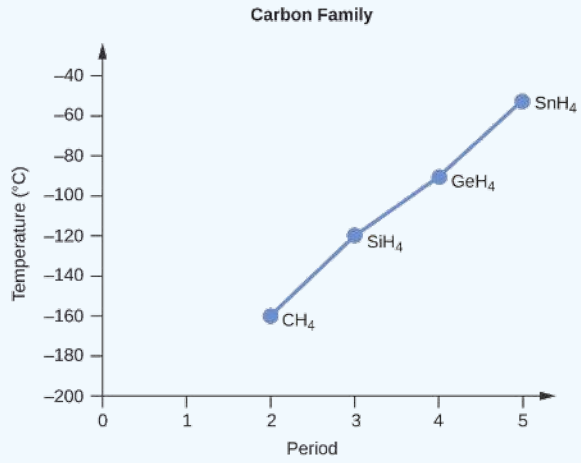
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: $CH_4$, $SiH_4$, $GeH_4$, and $SnH_4$. Explain your reasoning.

**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 elementsshows this prediction to be correct:




### Exercise 5.8.3

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

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

### 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.

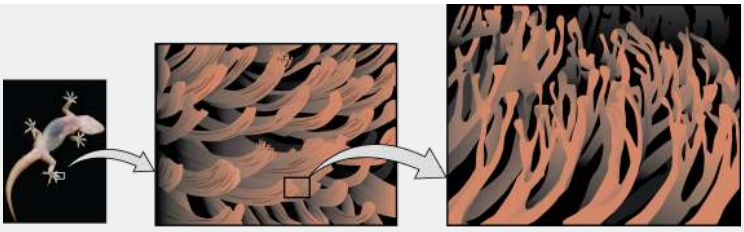



Figure 5.8.12: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos 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 5.8.3: 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 |
| $NH_3$ | hydrogen bonding | -33 |
| HF | hydrogen bonding | 20 |
| $H_2O$ | hydrogen bonding | 100 |

### Example 5.8.4: 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 5.8.4

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.

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# 5.9: Solids and Liquids

**Learning Objectives**

- To describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

## Solids

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



Figure 5.9.1: Crystalline Arrangement of Quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. from Wikipedia.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a crystal. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure 5.9.1. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

## Liquids

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



Figure 5.9.2: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. from Wikipedia.

## Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.

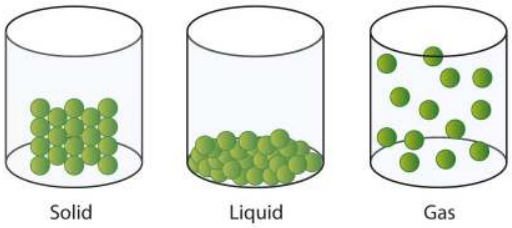



Figure 5.9.3: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figure 5.9.3 shows the differences among solids, liquids, and gases at the molecular level, while Table 5.9.1 lists the different characteristics of these states.

Table 5.9.1: Characteristics of the Three States of Matter

| Characteristic | Solid | Liquid | Gas |
|---|---|---|---|
| shape | definite | indefinite | indefinite |
| volume | definite | definite | indefinite |
| relative intermolecular interaction strength | strong | moderate | weak |
| relative particle positions | in contact and fixed in place | in contact but not fixed | not in contact, random positions |

### Example 5.9.1

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

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

**Solution**

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

### Exercise 5.9.1

What state or states of matter does each statement describe?

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

**Answer**

a. solid
b. gas
c. solid

## Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. The most energetically favorable configuration of $H_2O$ molecules is one in which each molecule is hydrogen-bonded to four neighboring molecules. Owing to the thermal motions, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.

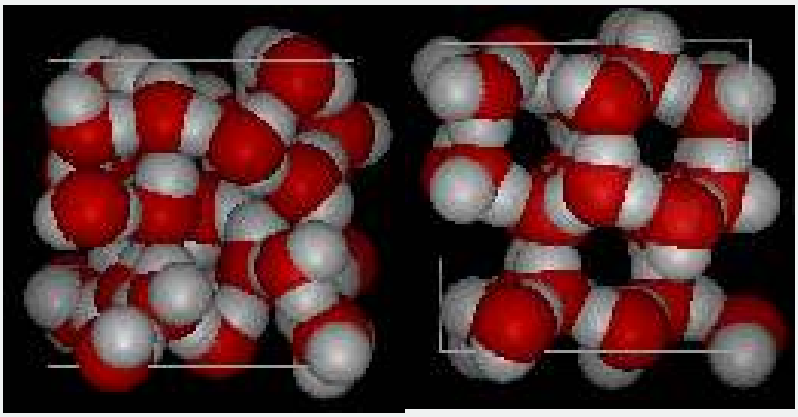


Figure **5.9.4**: Three-dimensional views of a typical local structure of liquid water (left) and ice (right).

Here are three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of hydrogen bonding in a uniform, extended crystal lattice. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion. Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of $H_2O$ by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water’s influence on the world around us is affected by these properties. Isn’t it fascinating that such a small molecule can have such a big impact?

## Key Takeaway

- Solids and liquids are phases that have their own unique properties.

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# 5.S: Covalent Bonding and Simple Molecular Compounds (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

Atoms can share pairs of valence electrons to obtain a valence shell octet. This sharing of electrons is a **covalent bond**. A species formed from covalently bonded atoms is a **molecule** and is represented by a **molecular formula**, which gives the number of atoms of each type in the molecule. The two electrons shared in a covalent bond are called a **bonding pair of electrons**. The electrons that do not participate in covalent bonds are called **nonbonding pairs** (or **lone pairs**) **of electrons**. A covalent bond consisting of one pair of shared electrons is called a **single bond**.

Covalent bonds occur between nonmetal atoms. Naming simple covalent compounds follows simple rules similar to those for ionic compounds. However, for covalent compounds, numerical prefixes are used as necessary to specify the number of atoms of each element in the compound.

In some cases, more than one pair of electrons is shared to satisfy the octet rule. Two pairs of electrons are shared by two atoms to make a **double bond**. Three pairs of atoms are shared to make a **triple bond**. Single, double, and triple covalent bonds may be represented by one, two, or three dashes, respectively, between the symbols of the atoms.

The distance between two covalently bonded atoms is the **bond length**. Bond lengths depend on the types of atoms participating in the bond as well as the number of electron pairs being shared. A covalent bond can be a **polar covalent bond** if the electron sharing between the two atoms is unequal. If the sharing is equal, the bond is a **nonpolar covalent bond**. Because the strength of an atom's attraction for electrons in a bond is rated by the atom's **electronegativity**, the difference in the two atoms' electronegativities indicates how polar a covalent bond between those atoms will be.

The shape of a molecule can be predicted using **valence shell electron pair repulsion (VSEPR)**, which uses the fact that the negative electrons in covalent bonds repel each other as much as possible. Molecules with polar bonds are **polar** except when the bond polarities cancel due to symmetry.

**Organic chemistry** is the chemistry of carbon compounds. Carbon forms covalent bonds with other carbon atoms and with the atoms of many other elements. The simplest organic compounds are **hydrocarbons**, which consist solely of carbon and hydrogen. Hydrocarbons containing only single bonds are called **alkanes (saturated hydrocarbons)**. Hydrocarbons containing carbon–carbon double bonds are **alkenes**, while hydrocarbons with carbon–carbon triple bonds are **alkynes**. Carbon-carbon double and triple bonds are examples of **functional groups**, atoms or bonds that impart a characteristic chemical function to the molecule. Other functional groups include the alcohol functional group (OH) and the **carboxyl functional group** (COOH). They are the characteristic functional group in organic compounds called **alcohols** and **carboxylic acids**.

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# CHAPTER OVERVIEW

## 6: Introduction to Chemical Reactions

Chemical change is a central concept in chemistry. The goal of chemists is to know how and why a substance changes in the presence of another substance or even by itself. Because there are tens of millions of known substances, there are a huge number of possible chemical reactions. In this chapter, we will find that many of these reactions can be classified into a small number of categories according to certain shared characteristics.


6.1: Prelude to Introduction to Chemical Reactions

6.2: The Law of Conservation of Matter

6.3: Chemical Equations

6.4: Some Types of Chemical Reactions

6.5: Types of Chemical Reactions - Single and Double Replacement Reactions

6.6: Oxidation-Reduction (Redox) Reactions

6.S: Introduction to Chemical Reactions (Summary)


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# 6.1: Prelude to Introduction to Chemical Reactions

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are single-celled fungi. About 1,000 species are recognized, but the most common species is *Saccharomyces cerevisiae*, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

Yeasts live primarily on sugars, such as glucose ($\mathrm{C_6H_{12}O_6}$). They convert glucose into carbon dioxide ($\mathrm{CO_2}$) and ethanol ($\mathrm{C_2H_5OH}$) in a chemical transformation that is represented as follows:

$$\mathrm{C_6H_{12}O_6\,(s) \longrightarrow 2\,CO_2\,(g) + 2\,C_2H_5OH(\ell)}$$

Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of yeast, fermentation, depends on the production of ethanol, which results from the same chemical transformation. Some alcoholic beverages, such as champagne, can also be carbonated using the carbon dioxide produced by the yeast.

Yeast is among the simplest life forms on Earth, yet it is absolutely necessary for at least two major food industries. Without yeast to turn dough into bread and juice into wine, these foods and food industries would not exist today.

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# 6.2: The Law of Conservation of Matter

**Learning Objectives**

- Correctly define a law as it pertains to science.
- State the law of conservation of matter.

In science, a law is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge. One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is *conserved*.

With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist A. Lavoisier laid the foundation to the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. These eventually formed the basis of Dalton's Atomic Theory of Matter.

## Law of Conservation of Mass

According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

$$\overbrace{\underbrace{HgO\,(s)}_{100\ g}}^{\text{Mercuric oxide}} \rightarrow \overbrace{\underbrace{Hg\,(l)}_{92.6\ g}}^{\text{Mercury}} + \overbrace{\underbrace{O_2\,(g)}_{7.4\ g}}^{\text{Oxygen}} \tag{6.2.1}$$

Another way of stating this is, "In a chemical reaction, matter is neither created nor destroyed." The law of conservation of mass is also known as the "law of indestructibility of matter."

**Example 6.2.1**

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



*A sample of calcium carbonate ($CaCO_3$). (Public Domain; Walkerma).*

**Solution**

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

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

What does this mean for chemistry? In any chemical change, one or more initial substances change into a different substance or substances. Both the initial and final substances are composed of atoms because all matter is composed of atoms. According to the

law of conservation of matter, matter is neither created nor destroyed, so we must have the **same number and kind of atoms** after the chemical change as were present before the chemical change.

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Figure 5.1.1 shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose we had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose we had been able to measure the oxygen used by the fire and the gases produced by the fire. What would we find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

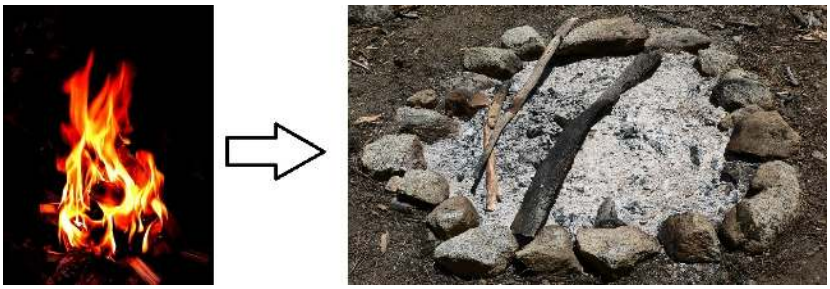


Figure 5.1.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

**Exercise 6.2.1**

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

**Answer a:**

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

**Answer b:**

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

## Key Takeaway

The amount of matter in a closed system is conserved.

## Contributors and Attributions

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# 6.3: Chemical Equations

**Learning Objectives**

- Define *chemical reaction*.
- Use a balanced chemical equation to represent a chemical reaction.

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 **6.3.1** shows a rather dramatic example of this very reaction.

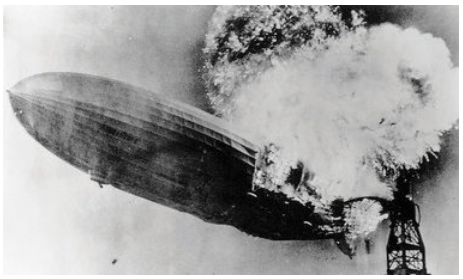


Figure **6.3.1**: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin *SS Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

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:

$$\mathbf{H_2 + O_2 \rightarrow H_2O} \tag{6.3.1}$$

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, ($\ell$) 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:

$$\mathbf{H_2\,(g) + O_2\,(g) \rightarrow H_2O\ (\ell)} \tag{6.3.2}$$

Chemical equations can also be used to describe physical changes. We will see examples of this soon.

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 **6.3.2**).

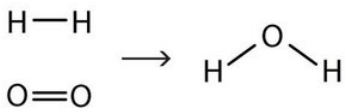



Figure **6.3.2**: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.

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:

$$\mathrm{H_2\,(g) + O_2\,(g)\ \rightarrow 2\,H_2O\ (\ell)} \tag{6.3.3}$$

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:

$$\mathrm{2\,H_2\,(g) + O_2\,(g)\ \rightarrow 2\,H_2O\ (\ell)} \tag{6.3.4}$$

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 **balanced** (Figure **6.3.3**). The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

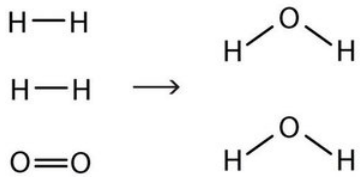



Figure **6.3.3**: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.

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

**Example 6.3.1**

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.

**Exercise 6.3.1**

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

How does one balance a chemical equation, starting with the correct formulas of the reactants and products? Basically, a **back-and-forth 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.

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + HCl} \tag{6.3.5}$$

*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 |

(6.3.6)

*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:

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{6.3.7}$$

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

(6.3.8)

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 $Cl_2$ reactant:

$$\mathrm{CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{6.3.9}$$

| Reactants | Products |
|---|---|
| 1 C atom | 1 C atom |
| 4 H ions | 4 H ions |
| 8 Cl atom | 8 Cl atoms |

(6.3.10)

*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 6.3.2**

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.

$$\mathrm{Pb(NO_3)_2}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{6.3.11}$$

*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 $NO_3^-$ ions | 1 $NO_3^-$ ions |
| 1 Na atom | 1 Na atom |
| 1 Cl atom | 2 Cl atoms |

(6.3.12)

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

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{NaCl}\,(aq) \rightarrow 2\mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{6.3.13}$$

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

| Reactants | Products |
|---|---|
| 1 Pb atom | 1 Pb atom |
| 2 $NO_3^-$ ions | 2 $NO_3^-$ ions |
| 2 Na atom | 2 Na atom |
| 2 Cl atom | 2 Cl atoms |

(6.3.14)

*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 6.3.2**

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**

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

## Concept Review Exercises

a. What are the parts of a chemical equation?

b. Explain why chemical equations need to be balanced.

## Answers

a. reactants and products

b. Chemical equations need to be balanced to satisfy the law of conservation of matter.

## Key Takeaway

Chemical reactions are represented by chemical equations that list reactants and products. Proper chemical equations are balanced; the same number of each element's atoms appears on each side of the equation.

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# 6.4: Some Types of Chemical Reactions

**Learning Objectives**

- To classify a given chemical reaction into a variety of types.

Although there are untold millions of possible chemical reactions, most can be classified into a small number of general reaction types. Classifying reactions has two purposes: it helps us to recognize similarities among them, and it enables us to predict the products of certain reactions. A particular reaction may fall into more than one of the categories that we will define in this book.

## Combination (composition) Reactions

A combination (composition) reaction is a chemical reaction that makes a single substance from two or more reactants. There may be more than one molecule of product in the balanced chemical equation, but there is only one substance produced. For example, the equation

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

is a combination reaction that produces $Fe_2O_3$ from its constituent elements—Fe and $O_2$. Combination reactions do not have to combine elements, however. The chemical equation

$$Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3$$

shows a combination reaction in which $Fe_2O_3$ combines with three molecules of $SO_3$ to make $Fe_2(SO_4)_3$.

**Example 6.4.1**

Which equations are combination reactions?

a. $Co(s) + Cl_2(g) \rightarrow CoCl_2(s)$
b. $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$
c. $N_2H_4(\ell) + O_2(g) \rightarrow N_2(g) + 2H_2O(\ell)$

**Solution**

a. This is a combination reaction.
b. This is a combination reaction. (The compound $COCl_2$ is called phosgene and, in the past, was used as a gassing agent in chemical warfare.)
c. This is not a combination reaction.

**Exercise 6.4.1**

Which equations are combination reactions?

a. $P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(g)$
b. $SO_3(\ell) + H_2O(\ell) \rightarrow H_2SO_4(\ell)$
c. $NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(\ell)$

**Answer**

a and b are combination reactions

## Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction. In a decomposition reaction, a single substance is converted into two or more products. There may be more than one molecule of the reactant, but there is only one substance initially. For example, the equation

$$2\,NaHCO_3\,(s) \rightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O\ (\ell)$$

is a decomposition reaction that occurs when $NaHCO_3$ is exposed to heat. Another example is the decomposition of $KClO_3$:

$$2\,KClO_3\,(s) \rightarrow 2\,KCl\,(s) + 3\,O_2\,(g)$$

This reaction was once commonly used to generate small amounts of oxygen in the chemistry lab.

> The decomposition reaction of $NaHCO_3$ is the reaction that occurs when baking soda is poured on a small kitchen fire. The intent is that the $H_2O$ and $CO_2$ produced by the decomposition will smother the flames.

## Combustion Reactions

A combustion reaction occurs when a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction. Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. An example is propane ($C_3H_8$), a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

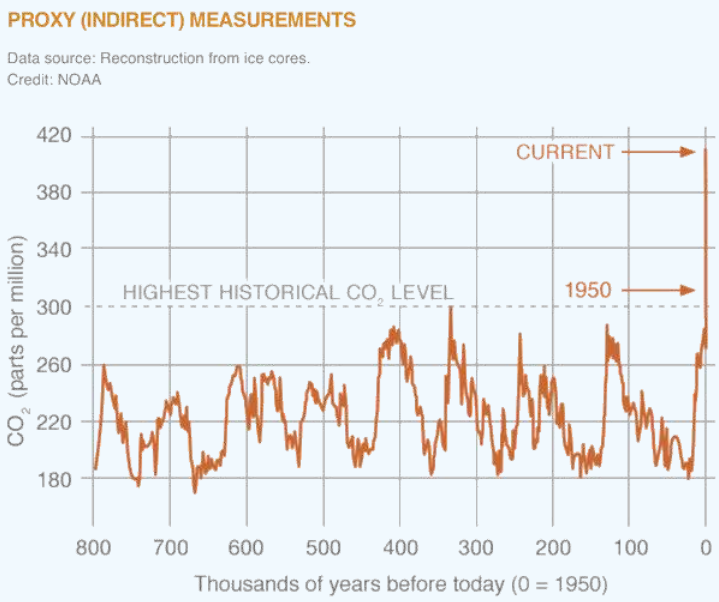
Another example is the burning of acetylene ($C_2H_2$) in welding torches:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O$$

Oxygen (in its elemental form) is a crucial reactant in combustion reactions.

> *Energy in the form of heat is usually given off as a product in a combustion reaction as well.*

**Example 6.4.2**




Carbon dioxide ($CO_2$) is an important heat-trapping (greenhouse) gas, which is released through human activities such as deforestation and burning fossil fuels, as well as natural processes such as respiration and volcanic eruptions. The graph above shows $CO_2$ levels during the last three glacial cycles, as reconstructed from ice cores.

Carbon dioxide is the primary greenhouse gas emitted through human activities. In 2015, $CO_2$ accounted for about 82.2% of all U.S. greenhouse gas emissions from human activities. Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle–both by adding more $CO_2$ to the atmosphere and by influencing the ability of natural

sinks, like forests, to remove $CO_2$ from the atmosphere. While $CO_2$ emissions come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution.

The main human activity that emits $CO_2$ is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit $CO_2$. An example of how $CO_2$ can be generated is the **combustion of octane** ($C_8H_{10}$), a component of gasoline.

Write the balanced equation to represent the combustion of octane.

**Solution**

$2C_8H_{10}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

The balanced reaction argues that for every two molecules of octane that are burned, 16 molecules of CO2 are generated.

## Example 6.4.2

Identify each type of reaction.

1. $2\,K(s) + S(s) + 2\,O_2(g) \longrightarrow K_2SO_4(s)$
2. $(NH_4)_2Cr_2O_7(s) \longrightarrow N_2(g) + Cr_2O_3(s) + 4\,H_2O(\ell)$
3. $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(\ell)$

**Solution**

1. Multiple reactants are combining to make a single product, so this reaction is a combination reaction.
2. A single substance reacts to make several products, so we have a decomposition reaction.
3. Oxygen reacts with a compound to make carbon dioxide (an oxide of carbon) and water (an oxide of hydrogen). This is a combustion reaction.

## Exercise 6.4.2

Identify each type of reaction.

a. $C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O$
b. $2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s)$
c. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

**Answer a**

combustion

**Answer b**

combination (also combustion)

**Answer c**

decomposition

## Concept Review Exercises

1. What is the difference between a combination reaction and a combustion reaction?
2. Give the distinguishing characteristic(s) of a decomposition reaction.
3. How do we recognize a combustion reaction?

## Answers

1. A combination reaction produces a certain substance; a combustion reaction is a vigorous reaction, usually a combination with oxygen, that is accompanied by the production of light and/or heat.
2. In a decomposition reaction, a single substance reacts to make multiple substances as products.

3. A combustion reaction is typically a vigorous reaction accompanied by light and/or heat, usually because of reaction with oxygen.

## Key Takeaway

There are several recognizable types of chemical reactions: combination, decomposition, and combustion reactions are examples.

## Exercises

1. Identify each type of reaction.
   a. $C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O$
   b. $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
   c. $C + 2H_2 \rightarrow CH_4$
2. Identify each type of reaction.
   a. $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
   b. $FeO + SO_3 \rightarrow FeSO_4$
   c. $CaCO_3(s) \rightarrow CO_2(g) + CaO(s)$
3. Identify each type of reaction.
   a. $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$
   b. $Hg(\ell) + ½O_2\ (g) \rightarrow HgO(s)$
   c. $CH_2CH_2(g) + Br_2(\ell) \rightarrow CH_2BrCH_2Br$
4. Identify each type of reaction.
   a. $Ti(s) + O_2(g) \rightarrow TiO_2(s)$
   b. $H_2SO_3(aq) \rightarrow H_2O(\ell) + SO_2(g)$
   c. $3O_2(g) \rightarrow 2O_3(g)$

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# 6.5: Types of Chemical Reactions - Single and Double Replacement Reactions

**Learning Objectives**

- Recognize chemical reactions as single-replacement reactions and double-replacement reactions.
- Use the periodic table, an activity series, or solubility rules to predict whether single-replacement reactions or double-replacement reactions will occur.

Up until now, we have presented chemical reactions as a topic, but we have not discussed how the products of a chemical reaction can be predicted. Here we will begin our study of certain types of chemical reactions that allow us to predict what the products of the reaction will be.

A **single-replacement reaction** is a chemical reaction in which one element is substituted for another element in a compound, generating a new element and a new compound as products. Presented below:

$$2\,HCl\,(aq) + Zn\,(s) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

is an example of a single-replacement reaction. The hydrogen atoms in **HCl** are replaced by **Zn** atoms, and in the process a new element—hydrogen—is formed. Another example of a single-replacement reaction is

$$2\,NaCl\,(aq) + F_2\,(g) \longrightarrow 2\,NaF\,(s) + Cl_2\,(g)$$

Here the negatively charged ion changes from chloride to fluoride. A typical characteristic of a single-replacement reaction is that there is one element as a reactant and another element as a product.

A **double-replacement reaction** occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products. An example is

$$CuCl_2\,(aq) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,AgCl\,(s)$$

There are two equivalent ways of considering a double-replacement equation: either the cations are swapped, or the anions are swapped. (You cannot swap both; you would end up with the same substances you started with.) Either perspective should allow you to predict the proper products, as long as you pair a cation with an anion, and not a cation with a cation or an anion with an anion.

**Example 6.5.3**

Predict the products of this double-replacement equation:

$$BaCl_2 + Na_2SO_4 \longrightarrow$$

**Solution**

Thinking about the reaction as either switching the cations or switching the anions, we would expect the products to be $BaSO_4$ and NaCl.

**Exercise 6.5.3**

Predict the products of this double-replacement equation:

$$KBr + AgNO_3 \longrightarrow$$

**Answer**

$KNO_3$ and AgBr

Predicting whether a double-replacement reaction occurs is somewhat more difficult than predicting a single-replacement reaction. However, there is one type of double-replacement reaction that we can predict: the precipitation reaction. A **precipitation reaction** occurs when two ionic compounds are dissolved in water and form a new ionic compound that does not dissolve; this new compound falls out of solution as a solid **precipitate.** The formation of a solid precipitate is the driving force that makes the reaction proceed.

## Key Takeaways

- A single-replacement reaction replaces one element for another in a compound.
- 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.

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# 6.6: Oxidation-Reduction (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 **6.6.1**):

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow H_2\,(g) + ZnCl_2\,(aq)} \tag{6.6.1}$$

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



Figure **6.6.1**: 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 6.6.1).

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq) \longrightarrow H_2\,(g) + Zn^{2+}\,(aq) + 2\,Cl^-\,(aq)}$$

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,

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)}$$

zinc atoms are oxidized to $Zn^{2+}$. The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:

$$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$$

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:

$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

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 6.6.1: 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:

$$Ag^+ + Al \longrightarrow Ag + Al^{3+}$$

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**:

$$Ag^+ + e^- \longrightarrow Ag$$

Aluminum is oxidized, losing three electrons to change from $Al$ to $Al^{3+}$:

**Oxidation half-reaction**:

$$Al \longrightarrow Al^{3+} + 3\,e^-$$

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: $\mathbf{Ag^+}$

## Exercise 6.6.1

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: $\mathbf{Ca^{2+} + 2\,e^- \longrightarrow Ca}$

Oxidation: \(2 \times (\ce{K -> K^{+} + e^{-}})\)

Combined: $\mathbf{Ca^{2+} + 2\,K \longrightarrow Ca + 2\,K^+}$

- The **substance oxidized** is the reactant that had undergone oxidation: $\mathbf{K}$
- The **substance reduced** is the reactant that had undergone reduction: $\mathbf{Ca^{2+}}$
- The **reducing agent** is the same as the substance oxidized: $\mathbf{K}$
- The **oxidizing agent** is the same as the substance reduced: $\mathbf{Ca^{2+}}$

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:

$$\mathbf{Cd\,(s) + 2\,NiOOH\,(s) + 2\,H_2O(\ell) \longrightarrow Cd(OH)_2\,(s) + 2\,Ni(OH)_2\,(s)}$$

The cadmium is oxidized, while the nickel atoms in $\mathbf{NiOOH}$ 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:

$$\mathbf{2\,Li\,(s) + I_2\,(s) \longrightarrow 2\,LiI\,(s)}$$

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 **6.6.1**: 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 ($CH_3COOH$).

$$2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH$$

Thus, acetaldehyde is being oxidized.

Similarly, **reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms**. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol ($CH_3CH_2OH$), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

Table shows how each process affects the change in oxygen and change in hydrogen.

| Process | Change in oxygen (some reactions) | Change in hydrogen (some reactions) |
|---|---|---|
| Oxidation | gain | lose |
| Reduction | lose | gain |

### Example 6.6.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $N_2 \longrightarrow NH_3$
b. $CH_3CH_2OHCH_3 \longrightarrow CH_3COCH_3$
c. $HCHO \longrightarrow HCOOH$

**Solution**

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

### Exercise 6.6.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $CH_4 \longrightarrow CO_2 + H_2O$
b. $NO_2 \longrightarrow N_2$
c. $CH_2{=}CH_2 \longrightarrow CH_3CH_3$

**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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# 6.S: Introduction to Chemical Reactions (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

Scientific **laws** are general statements that apply to a wide variety of circumstances. One important law in chemistry is the **law of conservation of matter**, which states that in any closed system, the amount of matter stays constant.

**Chemical equations** are used to represent **chemical reactions**. **Reactants** change chemically into **products**. The law of conservation of matter requires that a proper chemical equation be **balanced**. **Coefficients** are used to show the relative numbers of reactant and product molecules.

In **stoichiometry**, quantities of reactants and/or products can be related to each other using the balanced chemical equation. The coefficients in a balanced chemical reaction are used to devise the proper ratios that relate the number of molecules of one substance to the number of molecules of another substance.

Chemical reactions can be classified by type. **Combination reactions** (also called **composition reactions**) make a substance from other substances. **Decomposition reactions** break one substance down into multiple substances. **Combustion reactions** combine molecular oxygen with the atoms of another reactant.

**Oxidation reactions** are reactions in which an atom loses an electron. **Reduction reactions** are reactions in which an atom gains an electron. These two processes always occur together, so they are collectively referred to as **oxidation-reduction** (or **redox**) **reactions**. The species being oxidized it called the **reducing agent**, while the species being reduced is the **oxidizing agent**. Alternate definitions of oxidation and reduction focus on the gain or loss of oxygen atoms, or the loss or gain of hydrogen atoms. Redox reactions are easily balanced if the overall reaction is first separated into **half reactions**, which are individually balanced.

Oxidation-reduction reactions are common in organic and biological chemistry. **Respiration**, the process by which we inhale and metabolize oxygen, is a series of redox reactions. In the absence of oxygen, redox reactions still occur in a process called **anaerobic metabolism**. **Antioxidants** such as ascorbic acid also play a part in the human diet, acting as reducing agents in various biochemical reactions. **Photosynthesis**, the process by which plants convert water and carbon dioxide to glucose, is also based on redox reactions.

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# CHAPTER OVERVIEW

## 7: Organic Chemistry - Alkanes and Halogenated Hydrocarbons

We begin our study of organic chemistry with the alkanes, compounds containing only two elements, carbon and hydrogen, and having only single bonds. There are several other kinds of hydrocarbons, distinguished by the types of bonding between carbon atoms and by the properties that result from that bonding. We will first examine hydrocarbons with double bonds, with triple bonds, and with a special kind of bonding called aromaticity. Then we will study some compounds considered to be derived from hydrocarbons by replacing one or more hydrogen atoms with an oxygen-containing group. Finally, we focuse on organic acids and bases, after which we will be ready to look at the chemistry of life itself—biochemistry—in the remaining five chapters.


7.1: Prelude to Organic Chemistry - Alkanes and Halogenated Hydrocarbons
7.2: Organic Chemistry
7.3: Branched-Chain Alkanes
7.4: Structures and Names of Alkanes
7.5: Condensed Structural and Line-Angle Formulas
7.6: IUPAC Nomenclature
7.7: Halogenated Hydrocarbons
7.8: Cycloalkanes
7.9: Physical Properties of Alkanes
7.10: Chemical Properties of Alkanes
7.11: Organic Chemistry
7.12: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Summary)


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# 7.1: Prelude to Organic Chemistry - Alkanes and Halogenated Hydrocarbons

Hydrocarbons are the simplest organic compounds, but they have interesting physiological effects. These effects depend on the size of the hydrocarbon molecules and where on or in the body they are applied. Alkanes of low molar mass—those with from 1 to approximately 10 or so carbon atoms—are gases or light liquids that act as anesthetics. Inhaling ("sniffing") these hydrocarbons in gasoline or aerosol propellants for their intoxicating effect is a major health problem that can lead to liver, kidney, or brain damage or to immediate death by asphyxiation by excluding oxygen.

Swallowed, liquid alkanes do little harm while in the stomach. In the lungs, however, they cause "chemical" pneumonia by dissolving fatlike molecules from cell membranes in the tiny air sacs (alveoli). The lungs become unable to expel fluids, just as in pneumonia caused by bacteria or viruses. People who swallow gasoline or other liquid alkane mixtures should not be made to vomit, as this would increase the chance of getting alkanes into the lungs. (There is no home-treatment antidote for gasoline poisoning; call a poison control center.)



Figure **7.1.1**: Butane is a hydrocarbon with the formula $C_4H_{10}$ and is a gas at room temperature and atmospheric pressure. Under excess pressures, it can be liquidized like the fuel shown in this butane lighters. (CC BY-SA 3.0 Unported; Frank Vincentz via Wikipedia)

Liquid alkanes with approximately 5–16 carbon atoms per molecule wash away natural skin oils and cause drying and chapping of the skin, while heavier liquid alkanes (those with approximately 17 or more carbon atoms per molecule) act as emollients (skin softeners). Such alkane mixtures as mineral oil and petroleum jelly can be applied as a protective film. Water and aqueous solutions such as urine will not dissolve such a film, which explains why petroleum jelly protects a baby's tender skin from diaper rash.

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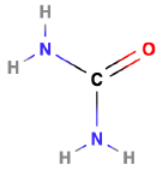
# 7.2: Organic Chemistry

**Learning Objectives**

- To recognize the composition and properties typical of organic and inorganic compounds.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride ($NH_4Cl$), expecting to get ammonium cyanate ($NH_4OCN$). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{7.2.1}$$

Instead, he found the product to be urea ($NH_2CONH_2$ or  ), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today organic chemistry is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table **7.2.1**.

Table **7.2.1**: General Contrasting Properties and Examples of Organic and Inorganic Compounds

| Organic | Hexane | | Inorganic | NaCl |
|---|---|---|---|---|
| low melting points | −95°C | | high melting points | 801°C |
| low boiling points | 69°C | | high boiling points | 1,413°C |
| low solubility in water; high solubility in nonpolar solvents | insoluble in water; soluble in gasoline | | greater solubility in water; low solubility in nonpolar solvents | soluble in water; insoluble in gasoline |
| flammable | highly flammable | | nonflammable | nonflammable |
| aqueous solutions do not conduct electricity | nonconductive | | aqueous solutions conduct electricity | conductive in aqueous solution |
| exhibit covalent bonding | covalent bonds | | exhibit ionic bonding | ionic bonds |

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table **7.2.1** also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane ($C_6H_{14}$), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table **7.2.1**.

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# 7.3: Branched-Chain Alkanes

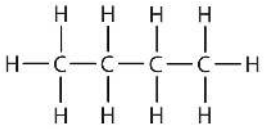
**Learning Objectives**

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

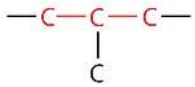
We can write the structure of butane ($C_4H_{10}$) by stringing four carbon atoms in a row,

–C–C–C–C–

and then adding enough hydrogen atoms to give each carbon atom four bonds:



The compound butane has this structure, 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 one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds.

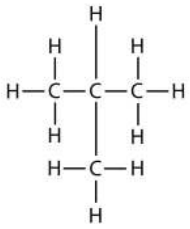


Figure **7.3.1**).

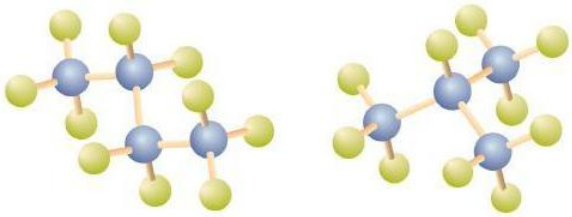
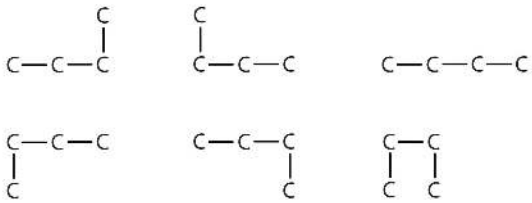


Figure **7.3.1**: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula $C_4H_{10}$.

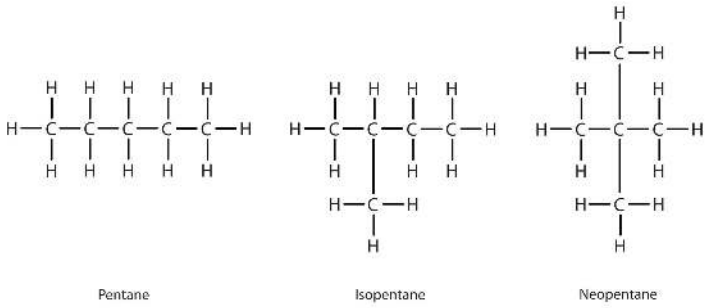
Notice that $C_4H_{10}$ is depicted with a bent chain in Figure **7.3.1**. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure **7.3.1**.

Unlike $C_4H_{10}$, the compounds methane ($CH_4$), ethane ($C_2H_6$), and propane ($C_3H_8$) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond $C_4H_{10}$ in the homologous series is pentane. Each compound has the same molecular formula: $C_5H_{12}$. (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) 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.




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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# 7.4: Structures and Names of Alkanes

**Learning Objectives**

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane ($CH_4$), ethane ($C_2H_6$), and propane ($C_3H_8$) and they are shown again in Figure **7.4.1**.

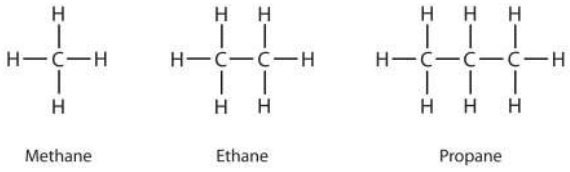



Figure **7.4.1**: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure **7.4.2**).

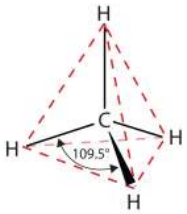



Figure **7.4.2**: The Tetrahedral Methane Molecule

Methane ($CH_4$), ethane ($C_2H_6$), and propane ($C_3H_8$) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a $CH_2$ unit. The first 10 members of this series are given in Table **7.4.1**.

Table **7.4.1**: The First 10 Straight-Chain Alkanes

| Name | Molecular Formula ($C_nH_{2n+2}$) | Condensed Structural Formula | Number of Possible Isomers |
|---|---|---|---|
| methane | $CH_4$ | $CH_4$ | — |
| ethane | $C_2H_6$ | $CH_3CH_3$ | — |
| propane | $C_3H_8$ | $CH_3CH_2CH_3$ | — |
| butane | $C_4H_{10}$ | $CH_3CH_2CH_2CH_3$ | 2 |
| pentane | $C_5H_{12}$ | $CH_3CH_2CH_2CH_2CH_3$ | 3 |
| hexane | $C_6H_{14}$ | $CH_3CH_2CH_2CH_2CH_2CH_3$ | 5 |
| heptane | $C_7H_{16}$ | $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ | 9 |
| octane | $C_8H_{18}$ | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | 18 |
| nonane | $C_9H_{20}$ | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | 35 |
| decane | $C_{10}H_{22}$ | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | 75 |

Consider the series in Figure **7.4.3**. The sequence starts with $C_3H_8$, and a $CH_2$ unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a $CH_2$ group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

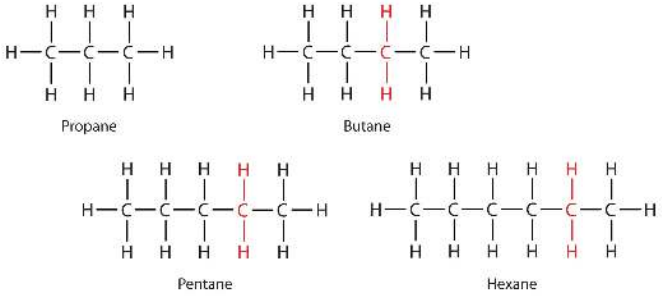



Figure **7.4.3**: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: $C_nH_{2n+2}$. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2\times 8)+2} = C_8H_{18}$.

## Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a $CH_2$ unit.

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# 7.5: Condensed Structural and Line-Angle Formulas

**Learning Objectives**

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula $C_4H_{10}$ tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:




The ultimate condensed formula is a line-angle formula, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:




Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

## Key Takeaways

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

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# 7.6: IUPAC Nomenclature

**Learning Objectives**

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

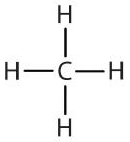
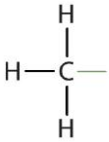
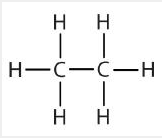
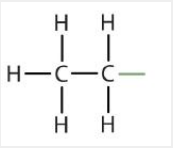
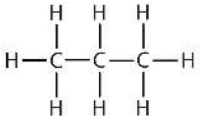
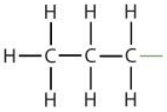
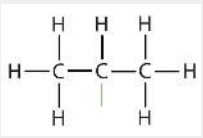
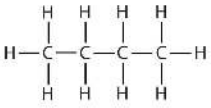
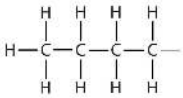
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table **7.6.1**) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table **7.6.1**: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

| Stem | Number |
|---|---|
| meth- | 1 |
| eth- | 2 |
| prop- | 3 |
| but- | 4 |
| pent- | 5 |
| hex- | 6 |
| hept- | 7 |
| oct- | 8 |
| non- | 9 |
| dec- | 10 |

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the $-CH_3$ group derived from methane ($CH_4$) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table **7.6.2**. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

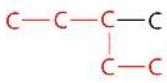
Table **7.6.2**: Common Alkyl Groups

| 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* |  | $CH_3CH_2CH_2CH_2–$ |

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example **7.6.1**).

1. **Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.
2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

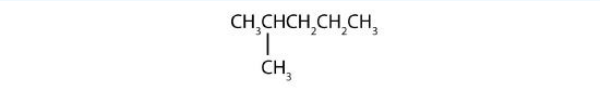
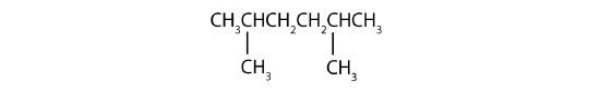
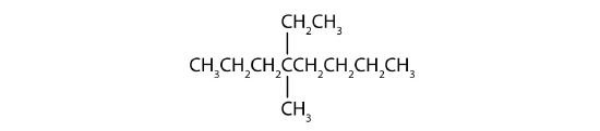


3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

## Example 7.6.1

Name each compound.

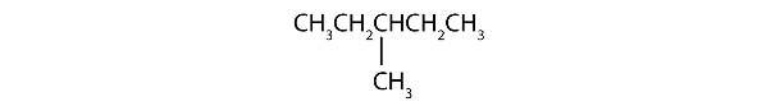
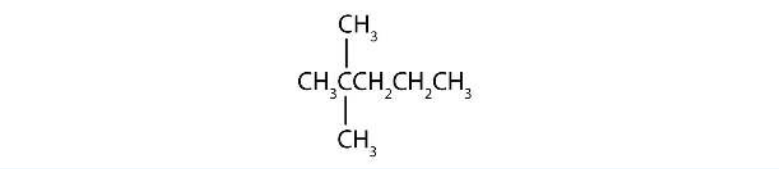
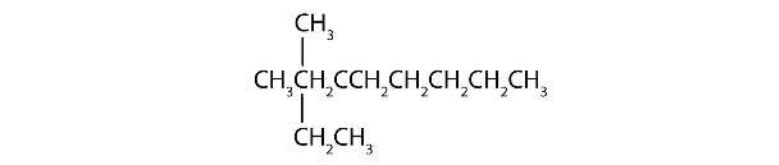
1. 
2. 
3. 

### Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexne (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

## Exercise 7.6.1

Name each compound.

1. 
2. 
3. 

## Example 7.6.2

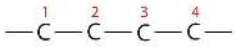
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

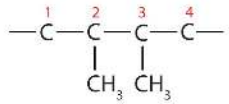
### Solution a

In drawing structures, always start with the parent chain.

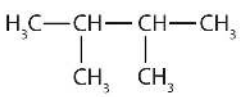
The parent chain is butane, indicating four carbon atoms in the LCC.



Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl ($CH_3$) groups, one on the second carbon atom and one on the third.

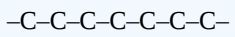


Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.

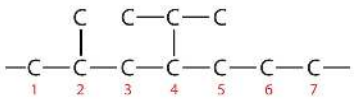


### Solution b

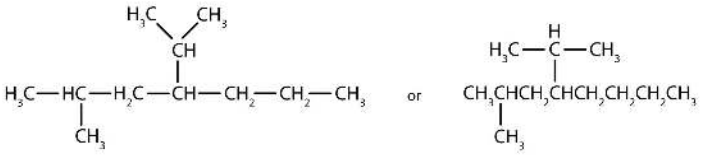
The parent chain is heptane in this case, indicating seven carbon atoms in the LCC.



Adding the groups at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas:



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

## Exercise 7.6.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

## Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

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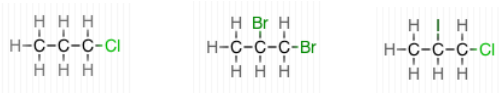
# 7.7: Halogenated Hydrocarbons

**Learning Objectives**

- To name halogenated hydrocarbons given formulas and write formulas for these compounds given names.

Many organic compounds are closely related to the alkanes. As we noted previously, alkanes react with halogens to produce halogenated hydrocarbons, the simplest of which have a single halogen atom substituted for a hydrogen atom of the alkane. Even more closely related are the cycloalkanes, compounds in which the carbon atoms are joined in a ring, or cyclic fashion.

The reactions of alkanes with halogens produce halogenated hydrocarbons, compounds in which one or more hydrogen atoms of a hydrocarbon have been replaced by halogen atoms:

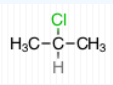


The replacement of only one hydrogen atom gives an alkyl halide (or haloalkane). The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*. The IUPAC system uses the name of the parent alkane with a prefix indicating the halogen substituents, preceded by number indicating the substituent's location. The prefixes are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. Thus $CH_3CH_2Cl$ has the common name ethyl chloride and the IUPAC name chloroethane. Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

**Example 7.7.1**

Give the IUPAC names for each compound.

a. $CH_3CH_2CH_2Br$

b. 

**Solution**

a. The molecule is a propane with a halogen bromine (Br). For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.

b. The molecule is a propane with a halogen chlorine (Cl) atom attached to the middle carbon atom. For the IUPAC name, the Cl atom (prefix *chloro-*) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

**Exercise 7.7.1**

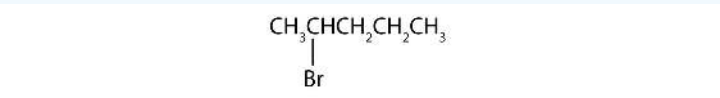
Give the IUPAC names for each compound.

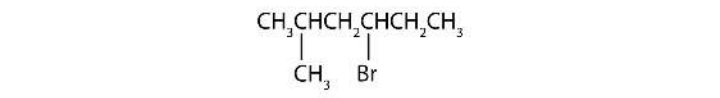
a. $CH_3CH_2I$

b. $CH_3CH_2CH_2CH_2F$

**Example 7.7.2**

Give the IUPAC name for each compound.

1. 

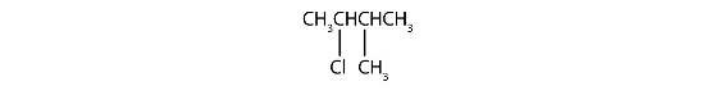
2. 

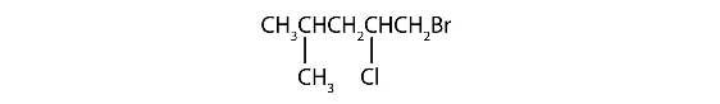
**Solution**

1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl ($CH_3$) and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

**Exercise 7.7.2**

Give the IUPAC name for each compound.

a. 

b. 

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 **7.7.1**, along with some of their uses.

Table **7.7.1**: 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 |

## 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.

## 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 **7.7.1**.

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.

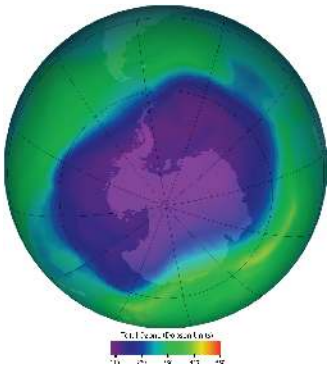


Figure **7.7.1**: Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas 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.

## Concept Review Exercises

1. What is the IUPAC name for the HFC that has the formula  ?(Hint: you must use a number to indicate the location of each substituent F atom.)

2. What is the IUPAC name for the HCFC that has the formula  ?

## Answers

1. 1,1,1,2-tetrafluoroethane
2. 2,2-dichloro-1,1,1-trifluoroethane

## Key Takeaway

- The replacement of an hydrogen atom on an alkane by a halogen atom—F, Cl, Br, or I—forms a halogenated compound.

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# 7.8: Cycloalkanes

**Learning Objectives**

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form *ring* or *cyclic* structures. The simplest of these cyclic hydrocarbons has the formula $C_3H_6$. Each carbon atom has two hydrogen atoms attached (Figure **7.8.1**) and is called cyclopropane.

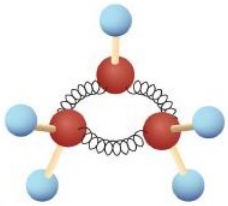
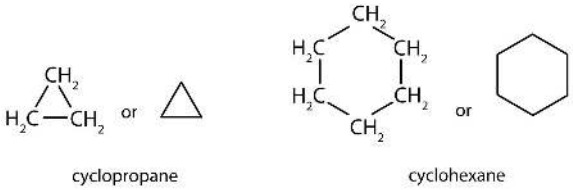


Figure **7.8.1**: Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.

## 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.

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 **7.8.1** interprets the name of a cycloalkane with a single substituent group.

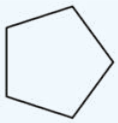
**Example 7.8.1**

Draw the structure for each compound.

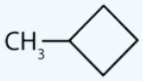
a. cyclopentane
b. methylcyclobutane

**Solution**

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



b. 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 7.8.1**

Draw the structure for each compound.

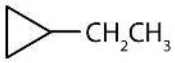
a. cycloheptane
b. ethylcyclohexane

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure 7.8.1.) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

## Concept Review Exercises

1. What is the molecular formula of cyclooctane?
2. What is the IUPAC name for this compound?



## Answers

1. $C_8H_{16}$
2. ethylcyclopropane

## Key Takeaway

- Many organic compounds have cyclic structures.

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# 7.9: Physical 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 **7.9.1** 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 **7.9.1**: 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 **7.9.1**: 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, http://www.nasa.gov/topics/earth/features/oilspill/oil-20100519a.html.

## Looking Closer: Gas Densities and Fire Hazards

Table **7.9.1** 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 **7.9.1** 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.

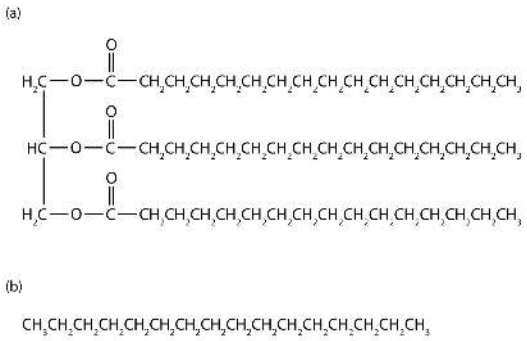



Figure **7.9.2**: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

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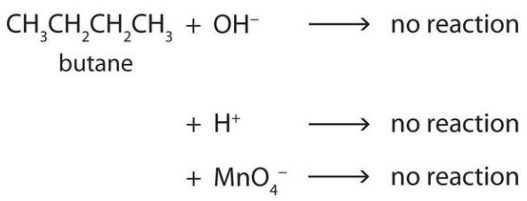
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# 7.10: Chemical Properties of Alkanes

**Learning Objectives**

- To identify the main chemical properties of alkanes.

Alkane molecules are nonpolar and therefore generally do not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents. Consider butane as an example:




Butane plus O H superscript negative sign yields no reaction. There is also no reaction of butane with H superscript positive sign and Mn O subscript 4 superscript negative sign.

Neither positive ions nor negative ions are attracted to a nonpolar molecule. In fact, the alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning "little affinity."

Two important reactions that the alkanes do undergo are combustion and halogenation. Nothing happens when alkanes are merely mixed with oxygen ($O_2$) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane ($CH_4$), the reaction is as follows:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + \text{heat}$$

If the reactants are adequately mixed and there is sufficient oxygen, the only products are carbon dioxide ($CO_2$), water ($H_2O$), and heat—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, however, other products are frequently formed. When the oxygen supply is limited, carbon monoxide ($CO$) is a by-product:

$$2\,CH_4 + 3\,O_2 \rightarrow 2\,CO + 4\,H_2O$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Alkanes also react with the halogens chlorine ($Cl_2$) and bromine ($Br_2$) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane ($CH_4$) to give methyl chloride ( $CH_3Cl$).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

With more chlorine, a mixture of products is obtained: $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, and $CCl_4$. Fluorine ($F_2$), the lightest halogen, combines explosively with most hydrocarbons. Iodine ($I_2$) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

## Key Takeaway

- Alkanes react with oxygen (combustion) and with halogens (halogenation).

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# 7.11: Organic Chemistry

**Learning Objectives**

- Define *organic chemistry*.
- Identify organic molecules as alkanes, alkenes, alkynes, alcohols, or carboxylic acids.

When methane was mentioned previously, we described it as the simplest organic compound. In this section, we introduce organic chemistry more formally. Organic chemistry is the study of the chemistry of carbon 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.

## Alkanes

The simplest organic compounds are the **hydrocarbons**, compounds composed of carbon and hydrogen atoms only. Some hydrocarbons have only single bonds and appear as a chain (which can be a straight chain or can have branches) of carbon atoms also bonded to hydrogen atoms. These hydrocarbons are called **alkanes (saturated hydrocarbons)**. Each alkane has a characteristic, systematic name depending on the number of carbon atoms in the molecule. These names consist of a stem that indicates the number of carbon atoms in the chain plus the ending -ane. The stem meth- means one carbon atom, so methane is an alkane with one carbon atom. Similarly, the stem eth- means two carbon atoms; ethane is an alkane with two carbon atoms. Continuing, the stem prop- means three carbon atoms, so propane is an alkane with three carbon atoms. The stem but- means four carbon atoms; butane is an alkane with four carbon atoms. Figure **7.11.1** gives the Lewis structures, condensed structural formulas and molecular formulas of the four simplest alkanes. In the **condensed structural formula**, the covalent bonds are understood to exist between each carbon and the hydrogens associated with it, as well as between carbon atoms.

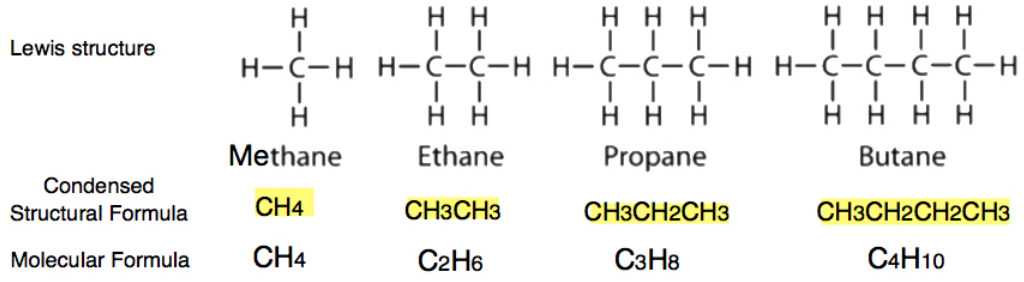



Figure **7.11.1**: Formulas and Molecular Models of the Four Simplest Alkanes. The four smallest alkanes are methane, ethane, propane and butane.

## Alkenes

Some hydrocarbons have one or more carbon–carbon double bonds (denoted C=C). These hydrocarbons are called alkenes. Figure **7.11.2** shows the formulas and the molecular models of the two simplest alkenes. Note that the names of alkenes have the same stem as the alkane with the same number of carbon atoms in its chain but have the ending *-ene*. Thus, ethene is an alkene with two carbon atoms per molecule, and propene is a compound with three carbon atoms and one double bond.

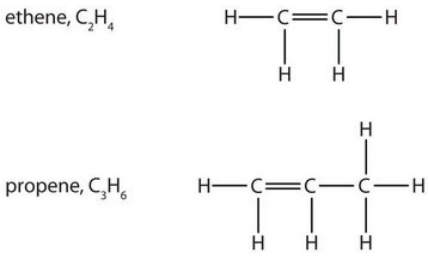
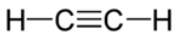



Figure **7.11.2**: Formulas and Molecular Models of the Two Simplest Alkenes. Ethene is commonly called ethylene, while propene is commonly called propylene.

## Alkynes

Alkynes are hydrocarbons with a carbon–carbon triple bond (denoted C≡C) as part of their carbon skeleton. Below is the formula and the molecular model of the simplest alkyne and its systematic name. Its common name is acetylene. Its chemical formula is $\mathbf{C_2H_2}$.



**Ethyne**

The names for alkynes have the same stems as for alkanes but with the ending *-yne*.

### To Your Health: Saturated and Unsaturated Fats

Hydrocarbons are not the only compounds that can have carbon–carbon double bonds. A group of compounds called fats can have them as well, and their presence or absence in the human diet is becoming increasingly correlated with health issues.

Fats are combinations of long-chain organic compounds (fatty acids) and glycerol ($C_3H_8O_3$). (For more information on fats, see Chapter 17) The long carbon chains can have either all single bonds, in which case the fat is classified as *saturated*, or one or more double bonds, in which case it is a *monounsaturated* or a *polyunsaturated* fat, respectively. Saturated fats are typically solids at room temperature; beef fat (tallow) is one example. Mono- or polyunsaturated fats are likely to be liquids at room temperature and are often called oils. Olive oil, flaxseed oil, and many fish oils are mono- or polyunsaturated fats.

Studies have linked higher amounts of saturated fats in people's diets with a greater likelihood of developing heart disease, high cholesterol, and other diet-related diseases. In contrast, increases in unsaturated fats (either mono- or polyunsaturated) have been linked to a lower incidence of certain diseases. Thus, there have been an increasing number of recommendations by government bodies and health associations to decrease the proportion of saturated fat and increase the proportion of unsaturated fat in the diet. Most of these organizations also recommend decreasing the total amount of fat in the diet.

Recently, certain fats called trans fats have been implicated in the presence of heart disease. These are fats from animal sources and are also produced when liquid oils are exposed to partial hydrogenation, an industrial process that increases their saturation. Trans fats are used in many prepared and fried foods. Because they bring with them the health risks that naturally occurring saturated fats do, there has been some effort to better quantify the presence of trans fats in food products. US law now requires that food labels list the amount of trans fat in each serving.

Since the early 1900's, the US Department of Agriculture has been providing science-based dietary guidelines for the public. The most current version is the MyPlate illustration that gives a simple, visual picture of how much of what kind of foods make up a good, balanced diet. It recommends minimizing daily intake of sugars, the "bad fats", trans and saturated fat, and sodium. "Good fats", unsaturated fats or oils, are not considered a food group but do contain essential nutrients and therefore are included as part of a healthy eating pattern. The difference as simple as the difference between a single and double carbon–carbon bond, good and bad fats, can have a significant impact on health.




MyPlate is a reminder that everything you eat and drink matters. Source: Image courtesy of the USDA, www.mypyramid.gov/downloads/MiniPoster.pdf.

## Functional Groups

The carbon–carbon double and triple bonds are examples of functional groups in organic chemistry. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to a molecule. Alkanes have no functional group. A carbon–carbon double bond is considered a functional group because carbon–carbon double bonds chemically react in specific ways that differ from reactions of alkanes (for example, under certain circumstances, alkenes react with water); a carbon–carbon triple bond also undergoes certain specific chemical reactions. In the remainder of this section, we introduce two other common functional groups.

If an OH group (also called a hydroxyl group) is substituted for a hydrogen atom in a hydrocarbon molecule, the compound is an alcohol. Alcohols are named using the parent hydrocarbon name but with the final *-e* dropped and the suffix *-ol* attached. The two simplest alcohols are methanol and ethanol. Figure **7.11.4** shows their formulas along with a molecular model of each.

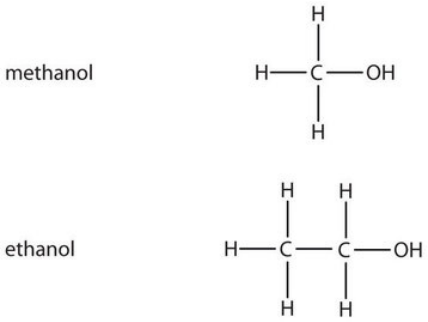



Figure **7.11.4**: The Two Simplest Organic Alcohol Compounds. Alcohols have an OH functional group in the molecule.

Cholesterol, described in the chapter-opening essay, has an alcohol functional group, as its name implies.

### Alcohol

Ethanol (also called ethyl alcohol) is the alcohol in alcoholic beverages. Other alcohols include methanol (or methyl alcohol), which is used as a solvent and a cleaner, and isopropyl alcohol (or rubbing alcohol), which is used as a medicinal disinfectant. Neither methanol nor isopropyl alcohol should be ingested, as they are toxic even in small quantities.

Another important family of organic compounds has a carboxyl group, in which a carbon atom is double-bonded to an oxygen atom and to an OH group. Compounds with a carboxyl functional group are called carboxylic acids, and their names end in *-oic acid*. Figure **7.11.5** shows the formulas and the molecular models of the two simplest carboxylic acids, perhaps best known by the common names formic acid and acetic acid. The carboxyl group is sometimes written in molecules as COOH.

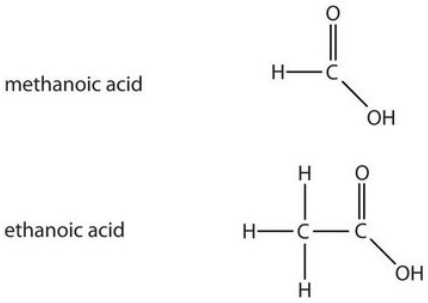


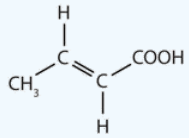

Figure **7.11.5**: The Two Smallest Organic Acids. The two smallest carboxylic acids are formic acid (found in the stingers of ants) and acetic acid (found in vinegar).

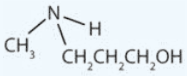
The condensed structures of methanoic acid and ethanoic acid are **HCOOH** and **$CH_3COOH$**, respectively.

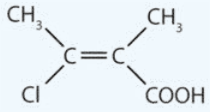
Many organic compounds are considerably more complex than the examples described here. Many compounds, such as cholesterol discussed in the chapter-opening essay, contain more than one functional group. The formal names can also be quite complex.

## Example 7.11.1

Identify the functional group(s) in each molecule as a double bond, a triple bond, an alcohol, or a carboxyl.

a. 

b. 

c. 

d. **$CH_3CH_2CH_2CH_2OH$**

**Answer a**

This molecule has a double bond and a carboxyl functional group.

**Answer b**

This molecule has an alcohol functional group.

**Answer c**

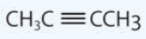
This molecule has a carbon-carbon double bond and a carboxyl functional group.

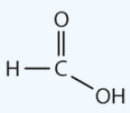
**Answer d**

This molecule has an alcohol functional group.

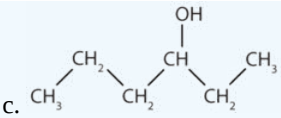
## Exercise 7.11.1

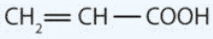
Identify the functional group(s) in each molecule as a double bond, a triple bond, an alcohol, or a carboxyl.

a. 

b. 


https://chem.libretexts.org/@go/page/289759

c. 

d. 

**Answer a:**

triple bond (alkyne)

**Answer b:**

carboxyl group

**Answer c:**

alcohol group

**Answer d:**

double bond (alkene) and carboxyl group

### Career Focus: Forensic Chemist

The main job of a forensic chemist is to identify unknown materials and their origins. Although forensic chemists are most closely associated in the public mind with crime labs, they are employed in pursuits as diverse as tracing evolutionary patterns in living organisms, identifying environmental contaminants, and determining the origin of manufactured chemicals.

In a crime lab, the forensic chemist has the job of identifying the evidence so that a crime can be solved. The unknown samples may consist of almost anything—for example, paint chips, blood, glass, cloth fibers, drugs, or human remains. The forensic chemist subjects them to a variety of chemical and instrumental tests to discover what the samples are. Sometimes these samples are extremely small, but sophisticated forensic labs have state-of-the-art equipment capable of identifying the smallest amount of unknown sample.

Another aspect of a forensic chemist's job is testifying in court. Judges and juries need to be informed about the results of forensic analyses, and it is the forensic chemist's job to explain those results. Good public-speaking skills, along with a broad background in chemistry, are necessary to be a successful forensic chemist.

## Key Takeaways

- Organic chemistry is the study of the chemistry of carbon compounds.
- Organic molecules can be classified according to the types of elements and bonds in the molecules.

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# 7.12: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the summary and ask yourself how they relate to the topics in the chapter.*

**Organic chemistry** is the chemistry of carbon compounds, and **inorganic chemistry** is the chemistry of all the other elements. Carbon atoms can form stable covalent bonds with other carbon atoms and with atoms of other elements, and this property allows the formation the tens of millions of organic compounds. **Hydrocarbons** contain only hydrogen and carbon atoms.

Hydrocarbons in which each carbon atom is bonded to four other atoms are called **alkanes** or **saturated hydrocarbons**. They have the general formula $C_nH_{2n+2}$. Any given alkane differs from the next one in a series by a $CH_2$ unit. Any family of compounds in which adjacent members differ from each other by a definite factor is called a **homologous series**.

Carbon atoms in alkanes can form straight chains or branched chains. Two or more compounds having the same molecular formula but different structural formulas are **isomers** of each other. There are no isomeric forms for the three smallest alkanes; beginning with $C_4H_{10}$, all other alkanes have isomeric forms.

A **structural formula** shows all the carbon and hydrogen atoms and how they are attached to one another. A **condensed structural formula** shows the hydrogen atoms right next to the carbon atoms to which they are attached. A **line-angle formula** is a formula in which carbon atoms are implied at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

The **IUPAC System of Nomenclature** provides rules for naming organic compounds. An **alkyl group** is a unit formed by removing one hydrogen atom from an alkane.

The physical properties of alkanes reflect the fact that alkane molecules are nonpolar. Alkanes are insoluble in water and less dense than water.

Alkanes are generally unreactive toward laboratory acids, bases, oxidizing agents, and reducing agents. They do burn (undergo **combustion reactions**).

Alkanes react with halogens by substituting one or more halogen atoms for hydrogen atoms to form **halogenated hydrocarbons**. An **alkyl halide (haloalkane)** is a compound resulting from the replacement of a hydrogen atom of an alkane with a halogen atom.

**Cycloalkanes** are hydrocarbons whose molecules are closed rings rather than straight or branched chains. A **cyclic hydrocarbon** is a hydrocarbon with a ring of carbon atoms

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# CHAPTER OVERVIEW

## 8: Unsaturated and Aromatic Hydrocarbons

Our modern society is based to a large degree on the chemicals we discuss in this chapter. Most are made from petroleum. Alkanes—saturated hydrocarbons—have relatively few important chemical properties other than that they undergo combustion and react with halogens. Unsaturated hydrocarbons—hydrocarbons with double or triple bonds—on the other hand, are quite reactive. In fact, they serve as building blocks for many familiar plastics—polyethylene, vinyl plastics, acrylics—and other important synthetic materials (e.g., alcohols, antifreeze, and detergents). Aromatic hydrocarbons have formulas that can be drawn as cyclic alkenes, making them appear unsaturated, but their structure and properties are generally quite different, so they are not considered to be alkenes. Aromatic compounds serve as the basis for many drugs, antiseptics, explosives, solvents, and plastics (e.g., polyesters and polystyrene). The two simplest unsaturated compounds—ethylene (ethene) and acetylene (ethyne)—were once used as anesthetics and were introduced to the medical field in 1924. However, it was discovered that acetylene forms explosive mixtures with air, so its medical use was abandoned in 1925. Ethylene was thought to be safer, but it too was implicated in numerous lethal fires and explosions during anesthesia. Even so, it remained an important anesthetic into the 1960s, when it was replaced by nonflammable anesthetics such as halothane ($CHBrClCF_3$).


8.1: Prelude to Unsaturated and Aromatic Hydrocarbons
8.2: Alkenes- Structures and Names
8.3: Cis-Trans Isomers (Geometric Isomers)
8.4: Physical Properties of Alkenes
8.5: Chemical Properties of Alkenes
8.6: Polymers
8.7: Alkynes
8.8: Aromatic Compounds- Benzene
8.9: Structure and Nomenclature of Aromatic Compounds
8.S: Unsaturated and Aromatic Hydrocarbons (Summary)


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# 8.1: Prelude to Unsaturated and Aromatic Hydrocarbons

Our modern society is based to a large degree on the chemicals we discuss in this chapter. Most are made from petroleum. Alkanes—saturated hydrocarbons—have relatively few important chemical properties other than that they undergo combustion and react with halogens. Unsaturated hydrocarbons—hydrocarbons with double or triple bonds—on the other hand, are quite reactive. In fact, they serve as building blocks for many familiar plastics—polyethylene, vinyl plastics, acrylics—and other important synthetic materials (e.g., alcohols, antifreeze, and detergents). Aromatic hydrocarbons have formulas that can be drawn as cyclic alkenes, making them appear unsaturated, but their structure and properties are generally quite different, so they are not considered to be alkenes. Aromatic compounds serve as the basis for many drugs, antiseptics, explosives, solvents, and plastics (e.g., polyesters and polystyrene).

The two simplest unsaturated compounds—ethylene (ethene) and acetylene (ethyne)—were once used as anesthetics and were introduced to the medical field in 1924. However, it was discovered that acetylene forms explosive mixtures with air, so its medical use was abandoned in 1925. Ethylene was thought to be safer, but it too was implicated in numerous lethal fires and explosions during anesthesia. Even so, it remained an important anesthetic into the 1960s, when it was replaced by nonflammable anesthetics such as halothane ($CHBrClCF_3$).

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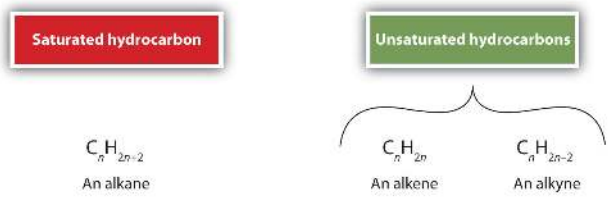
- **13.0: Prelude to Unsaturated and Aromatic Hydrocarbons** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.

# 8.2: Alkenes- Structures and Names

**Learning Objectives**

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

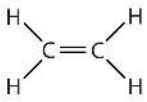



Some representative alkenes—their names, structures, and physical properties—are given in Table 8.2.1.

Table 8.2.1: Physical Properties of Some Selected Alkenes

| IUPAC Name | Molecular Formula | Condensed Structural Formula | Melting Point (°C) | Boiling Point (°C) |
|---|---|---|---|---|
| ethene | $C_2H_4$ | $CH_2{=}CH_2$ | –169 | –104 |
| propene | $C_3H_6$ | $CH_2{=}CHCH_3$ | –185 | –47 |
| 1-butene | $C_4H_8$ | $CH_2{=}CHCH_2CH_3$ | –185 | –6 |
| 1-pentene | $C_5H_{10}$ | $CH_2{=}CH(CH_2)_2CH_3$ | –138 | 30 |
| 1-hexene | $C_6H_{12}$ | $CH_2{=}CH(CH_2)_3CH_3$ | –140 | 63 |
| 1-heptene | $C_7H_{14}$ | $CH_2{=}CH(CH_2)_4CH_3$ | –119 | 94 |
| 1-octene | $C_8H_{16}$ | $CH_2{=}CH(CH_2)_5CH_3$ | –102 | 121 |

We used only condensed structural formulas in Table 8.2.1. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is $C_2H_4$, whereas that for ethane is $C_2H_6$.

The first two alkenes in Table 8.2.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 8.2.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

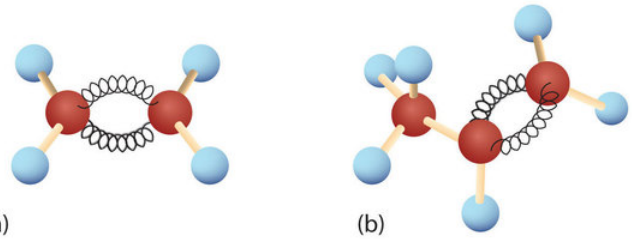
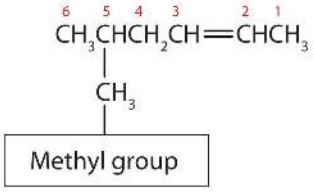



Figure **8.2.1**: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula $C_2H_4$ (ethene) and only one with the formula $C_3H_6$ (propene), there are several alkenes with the formula $C_4H_8$.

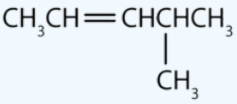
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

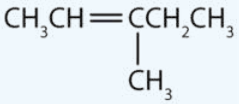
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2$=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound $CH_3CH$=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*




**Example 8.2.1**

Name each compound.

a. 

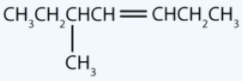
b. 

**Solution**

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

**Exercise 8.2.1**

Name each compound.

1. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$
2. 

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

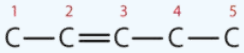
**Example 8.2.2**

Draw the structure for each compound.

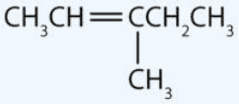
1. 3-methyl-2-pentene
2. cyclohexene

**Solution**

1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:



Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



2. First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



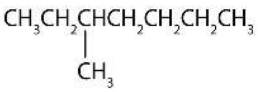
**Exercise 8.2.2**

Draw the structure for each compound.

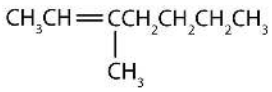
a. 2-ethyl-1-hexene
b. cyclopentene

## Concept Review Exercises

1. Briefly identify the important distinctions between a saturated hydrocarbon and an unsaturated hydrocarbon.
2. Briefly identify the important distinctions between an alkene and an alkane.
3. Classify each compound as saturated or unsaturated. Identify each as an alkane, an alkene, or an alkyne.



a.
b. $CH_3CH_2C{\equiv}CCH_3$

c. 

## Answers

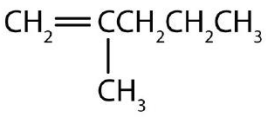
1. Unsaturated hydrocarbons have double or triple bonds and are quite reactive; saturated hydrocarbons have only single bonds and are rather unreactive.
2. An alkene has a double bond; an alkane has single bonds only.
3. a. saturated; alkane
   b. unsaturated; alkyne
   c. unsaturated; alkene

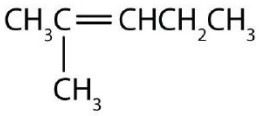
## Key Takeaway

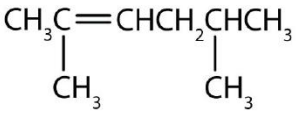
- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

## Exercises

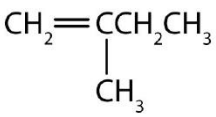
1. Draw the structure for each compound.
   a. 2-methyl-2-pentene
   b. 2,3-dimethyl-1-butene
   c. cyclohexene
2. Draw the structure for each compound.
   a. 5-methyl-1-hexene
   b. 3-ethyl-2-pentene
   c. 4-methyl-2-hexene
3. Name each compound according to the IUPAC system.

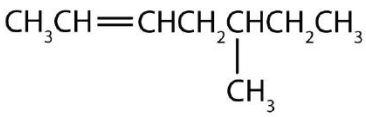
a. 

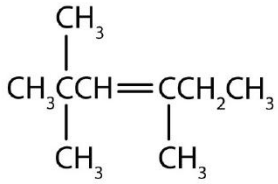
b. 

c. 

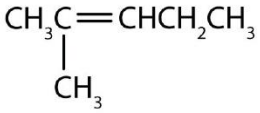
4. Name each compound according to the IUPAC system.

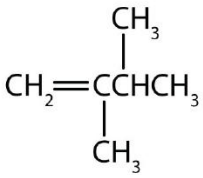
a. 

b. 

c. 

## Answers

1. a. 

   b. 

   c. 

3. a. 2-methyl-1-pentene
   b. 2-methyl-2-pentene
   c. 2,5-dimethyl-2-hexene

---

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# 8.3: Cis-Trans Isomers (Geometric Isomers)

**Learning Objectives**

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure **8.3.1**.

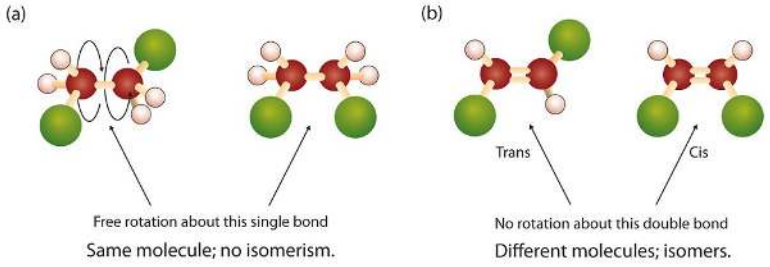



***Figure* 8.3.1***: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.*

In 1,2-dichloroethane (part (a) of Figure **8.3.1**), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:




In 1,2-dichloroethene (Figure **8.3.1***b*), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure **8.3.2**).

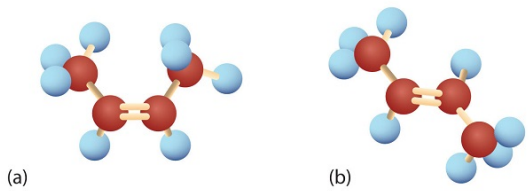



Figure **8.3.2**: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

*Cis*-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:




***Figure* 8.3.3**: *Models of (left) Cis-2-Butene and (right) Trans-2-Butene.*

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure **8.3.4**). We can draw two *seemingly* different propenes:




***Figure* 8.3.4**: *Different views of the propene molecule (flip vertically). These are not isomers.*

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C{=}CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C{=}CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

**Advanced Note: E/Z Isomerization**

If a molecule has a C=C bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature descried above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a C=C bond, with a methyl group and a bromine on one carbon , and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced E/Z nomenclature discussed elsewhere.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon–carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



**Example 8.3.1**

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. CHCl=CHBr
2. $CH_2$=$CBrCH_3$
3. $(CH_3)_2C$=$CHCH_2CH_3$
4. $CH_3CH$=$CHCH_2CH_3$

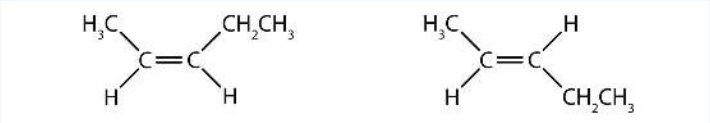
**Solution**

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:

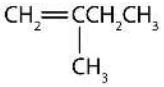


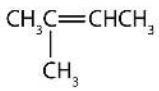

2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl ($CH_3$) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:




**Exercise 8.3.1**

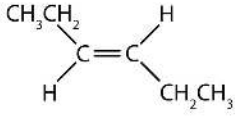
Which compounds can exist as cis-trans isomers? Draw them.

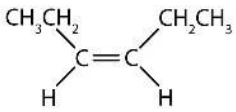
a. $CH_2$=$CHCH_2CH_2CH_3$
b. $CH_3CH$=$CHCH_2CH_3$
c. $CH_3CH_2CH$=$CHCH_2CH_3$
d. 

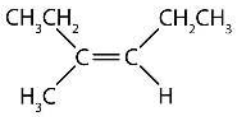
e. 

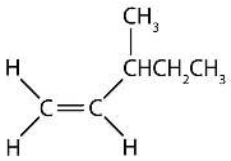

## Concept Review Exercises

1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?
2. Classify each compound as a cis isomer, a trans isomer, or neither.

a. 


b. 

c. 

d. 

## Answers

1. Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.

2. a. trans (the two hydrogen atoms are on opposite sides)
   b. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups)
   c. cis (the two ethyl groups are on the same side)
   d. neither (fliping the bond does not change the molecule. There are no isomers for this molecule)

## Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.

## Exercises

1. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.

   a. 2-bromo-2-pentene
   b. 3-hexene
   c. 4-methyl-2-pentene
   d. 1,1-dibromo-1-butene

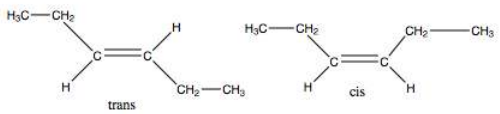
2. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.

   a. 2,3-dimethyl-2-pentene
   b. 5-methyl-2-hexene

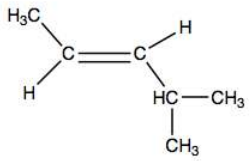
## Answer

1. a: none. There are two distinct geometric isomers, but since there are there are four different groups off the double bond, these are both cis/trans isomers (they are technically E/Z isomers discussed elsewhere).

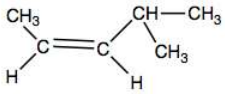
   b:




   c:




trans




cis

d: None

---

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# 8.4: Physical Properties of Alkenes

**Learning Objectives**

- To identify the physical properties of alkenes and describe trends in these properties.

The physical properties of alkenes are similar to those of the alkanes. The table at the start of the chapter shows that the boiling points of straight-chain alkenes increase with increasing molar mass, just as with alkanes. For molecules with the same number of carbon atoms and the same general shape, the boiling points usually differ only slightly, just as we would expect for substances whose molar mass differs by only 2 u (equivalent to two hydrogen atoms). Like other hydrocarbons, the alkenes are insoluble in water but soluble in organic solvents.

## Looking Closer: Environmental Note

Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Fruit processors artificially introduce ethylene to hasten the ripening process; exposure to as little as 0.1 mg of ethylene for 24 h can ripen 1 kg of tomatoes. Unfortunately, this process does not exactly duplicate the ripening process, and tomatoes picked green and treated this way don't taste much like vine-ripened tomatoes fresh from the garden.



*The bright red color of tomatoes is due to lycopene—a polyene.*

Other alkenes that occur in nature include 1-octene, a constituent of lemon oil, and octadecene ($C_{18}H_{36}$) found in fish liver. Dienes (two double bonds) and polyenes (three or more double bonds) are also common. Butadiene ($CH_2$=$CHCH$=$CH_2$) is found in coffee. Lycopene and the carotenes are isomeric polyenes ($C_{40}H_{56}$) that give the attractive red, orange, and yellow colors to watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A, essential to good vision, is derived from a carotene. The world would be a much less colorful place without alkenes.

## Concept Review Exercises

1. Briefly describe the physical properties of alkenes. How do these properties compare to those of the alkanes?
2. Without consulting tables, arrange the following alkenes in order of increasing boiling point: 1-butene, ethene, 1-hexene, and propene.

## Answers

1. Alkenes have physical properties (low boiling points, insoluble in water) quite similar to those of their corresponding alkanes.
2. ethene < propene < 1-butene < 1-hexene

## Key Takeaway

- The physical properties of alkenes are much like those of the alkanes: their boiling points increase with increasing molar mass, and they are insoluble in water.

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# 8.5: Chemical Properties of Alkenes

**Learning Objectives**

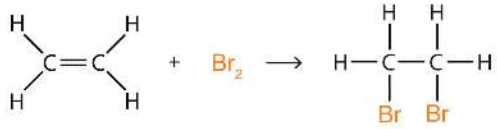
- To write equations for the addition reactions of alkenes with hydrogen, halogens, and water

Alkenes are valued mainly for addition reactions, in which one of the bonds in the double bond is broken. Each of the carbon atoms in the bond can then attach another atom or group while remaining joined to each other by a single bond. Perhaps the simplest addition reaction is hydrogenation—a reaction with hydrogen ($H_2$) in the presence of a catalyst such as nickel (Ni) or platinum (Pt).

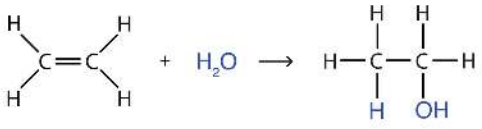



The product is an alkane having the same carbon skeleton as the alkene.

Alkenes also readily undergo halogenation—the addition of halogens. Indeed, the reaction with bromine ($Br_2$) can be used to test for alkenes. Bromine solutions are brownish red. When we add a $Br_2$ solution to an alkene, the color of the solution disappears because the alkene reacts with the bromine:




Another important addition reaction is that between an alkene and water to form an alcohol. This reaction, called hydration, requires a catalyst—usually a strong acid, such as sulfuric acid ($H_2SO_4$):




The hydration reaction is discussed later, where we deal with this reaction in the synthesis of alcohols.

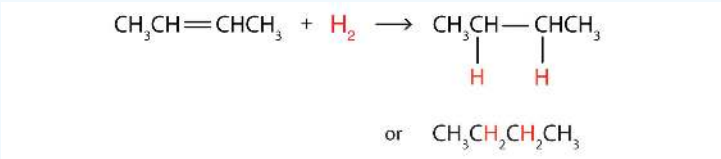
**Example 8.5.1**

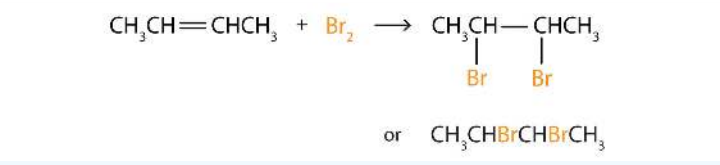
Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and each substance.

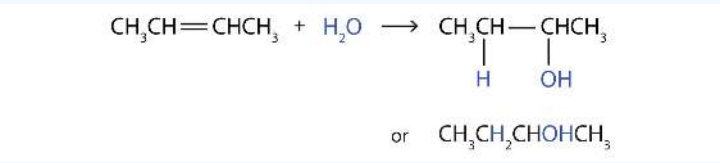
a. $H_2$ (Ni catalyst)
b. $Br_2$
c. $H_2O$ ($H_2SO_4$ an acid catalyst, $H^+$)

**Solution**

In each reaction, the reagent adds across the double bond.

a. 

b. 


c. 


**Exercise 8.5.1**

Write the equation for each reaction.

a. $CH_3CH_2CH{=}CH_2$ with $H_2$ (Ni catalyst)
b. $CH_3CH{=}CH_2$ with $Cl_2$
c. $CH_3CH_2CH{=}CHCH_2CH_3$ with $H_2O$ ($H_2SO_4$ catalyst)

## Concept Review Exercises

1. What is the principal difference in properties between alkenes and alkanes? How are they alike?
2. If $C_{12}H_{24}$ reacts with $Br_2$ in an addition reaction, what is the molecular formula of the product?

## Answers

1. Alkenes undergo addition reactions; alkanes do not. Both burn.
2. $C_{12}H_{24}Br_2$

## Key Takeaway

- Alkenes undergo addition reactions, adding such substances as hydrogen, bromine, and water across the carbon-to-carbon double bond.

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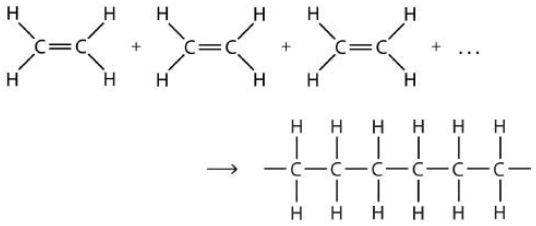
# 8.6: Polymers

**Learning Objectives**

- To draw structures for monomers that can undergo addition polymerization and for four-monomer-unit sections of an addition polymer.

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning “one,” and *meros*, meaning “parts”), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning “many,” and *meros*, meaning “parts”). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



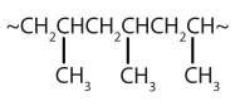
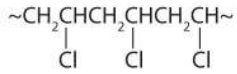
The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \text{–}\mathrm{CH_2CH_2}\text{–}_n$$

Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table **8.6.1**. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table **8.6.1***: Some Addition Polymers*

| Monomer | Polymer | Polymer Name | Some Uses |
|---|---|---|---|
| $CH_2=CH_2$ | ~$CH_2CH_2CH_2CH_2CH_2CH_2$~ | polyethylene | plastic bags, bottles, toys, electrical insulation |
| $CH_2=CHCH_3$ |  | polypropylene | carpeting, bottles, luggage, exercise clothing |
| $CH_2=CHCl$ |  | polyvinyl chloride | bags for intravenous solutions, pipes, tubing, floor coverings |
| $CF_2=CF_2$ | ~$CF_2CF_2CF_2CF_2CF_2CF_2$~ | polytetrafluoroethylene | nonstick coatings, electrical insulation |

### Medical Uses of Polymers

- An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

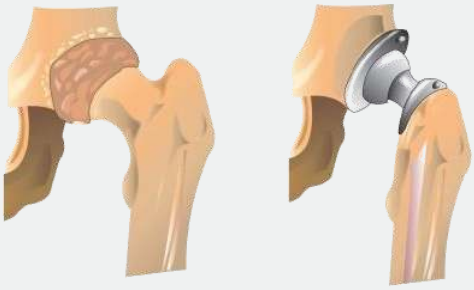


Figure **8.6.1**: Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

## Concept Review Exercises

1. What is a monomer? What is a polymer? How do polymer molecules differ from the molecules we have discussed in earlier sections of this chapter?
2. What is addition polymerization? What structural feature usually characterizes molecules used as monomers in addition polymerization?

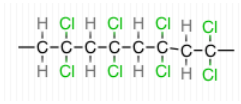
## Answers

1. Monomers are small molecules that can be assembled into giant molecules referred to as polymers, which are much larger than the molecules we discussed earlier in this chapter.
2. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers.

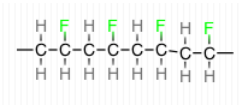
## Key Takeaway

- Molecules having carbon-to-carbon double bonds can undergo addition polymerization.

## Exercises

1. What is the name of the monomer from which Saran is formed. A segment of the Saran molecule has the following structure: $CH_2CCl_2C$ 
2. Write the condensed structural formula for the section of a molecule formed from four units of the monomer $CH_2$=CHF.

## Answers

1. $H_2C=CCl_2$ , 1,1-dichloroethene, 
2. 

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# 8.7: Alkynes

**Learning Objectives**

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula $C_2H_2$ and is known by its common name—acetylene (Figure **8.7.1**). Its structure is H–C≡C–H.

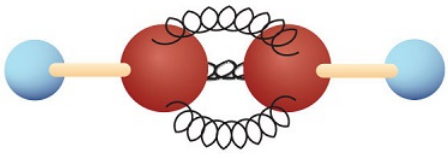


Figure **8.7.1**: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

## Key Takeaway

- Alkynes are hydrocarbons with carbon-to-carbon triple bonds and properties much like those of alkenes.

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# 8.8: Aromatic Compounds- Benzene

**Learning Objectives**

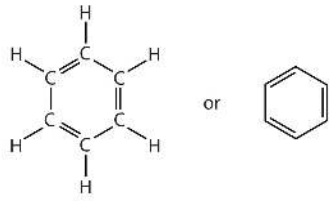
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene ($C_6H_6$) is of great commercial importance, but it also has noteworthy health effects.

The formula $C_6H_6$ seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula $C_6H_{14}$—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:




However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

**To Your Health: Benzene and Us**

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or

heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

## Concept Review Exercises

1. Briefly describe the bonding in benzene.
2. What does the circle mean in the chemist's representation of benzene?

## Answers

1. Valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized).
2. The six electrons are shared equally by all six carbon atoms.

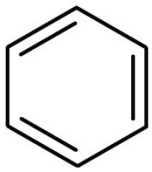
## Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

## Exercises

1. Draw the structure of benzene as if it had alternate single and double bonds.
2. Draw the structure of benzene as chemists usually represent it today.

## Answer

1. 

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# 8.9: Structure and Nomenclature of Aromatic Compounds

**Learning Objectives**

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

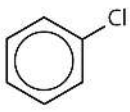
Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table 8.9.1, where the benzene ring is represented as $C_6H_5$.

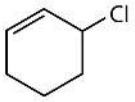
Table **8.9.1***: Some Representative Aromatic Compounds*

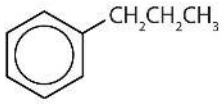
| Name | Structure | Typical Uses |
|---|---|---|
| aniline | $C_6H_5–NH_2$ | starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber |
| benzoic acid | $C_6H_5–COOH$ | food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco |
| bromobenzene | $C_6H_5–Br$ | starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive |
| phenol | $C_6H_5–OH$ | disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds |
| toluene or methylbenzene | $C_6H_5–CH_3$ | solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds |

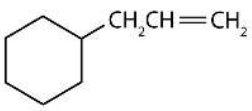
**Example 8.9.1**

Which compounds are aromatic?

1. 

2. 

3. 

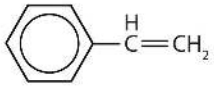
4. 

**Solution**

1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

**Exercise 8.9.1**

Which compounds are aromatic?

1. 
2. 
3. 

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 8.9.1 shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

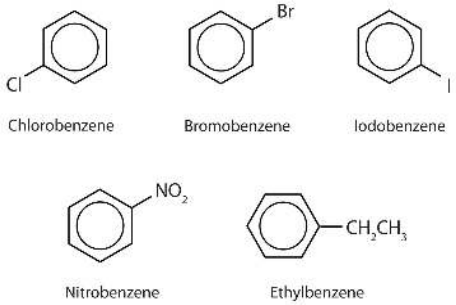



Figure 8.9.1: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, $NO_2$ as nitro, and $CH_3CH_2$ as ethyl.

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 8.9.1.




When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure 8.9.2). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.

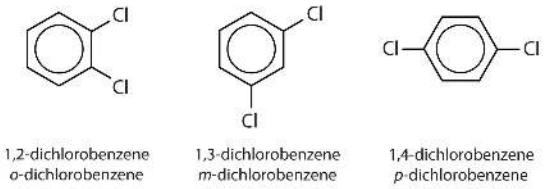
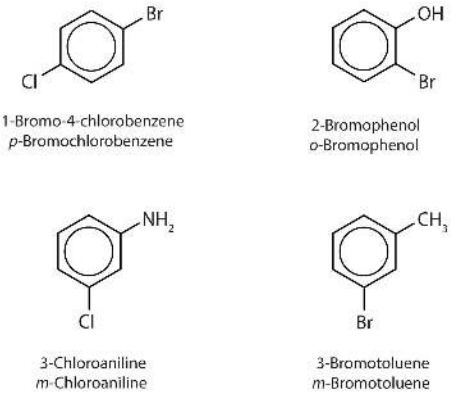


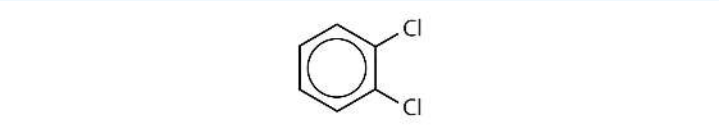

Figure **8.9.2**: The Three Isomeric Dichlorobenzenes

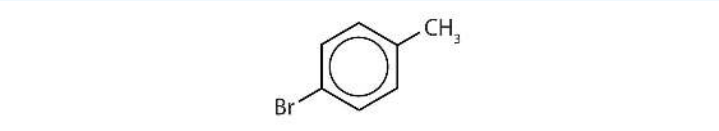
In Figure **8.9.2**, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:




**Example 8.9.2**

Name each compound using both the common name and the IUPAC name.

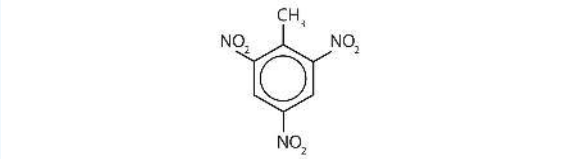
1. 


2. 


**Solution**

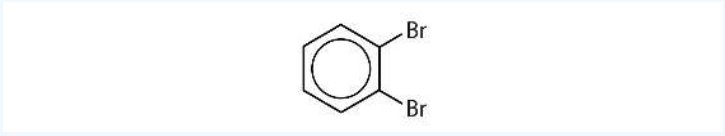
1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl ($CH_3$) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.

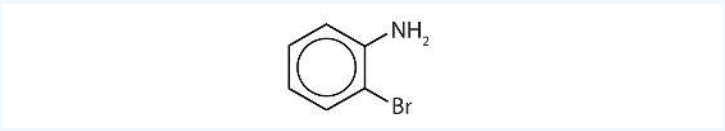
Note: The nitro ($NO_2$) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).

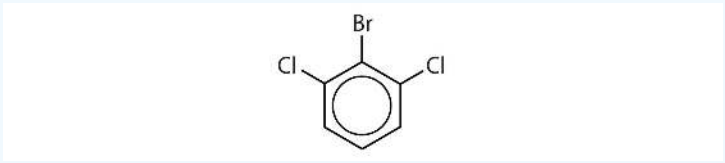


**Exercise 8.9.2**

Name each compound using both the common name and the IUPAC name.

1. 


2. 


3. 


Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene ($C_6H_6$) by removing one hydrogen atom ($C_6H_5$) and is called a *phenyl* group, from *pheno*, an old name for benzene.



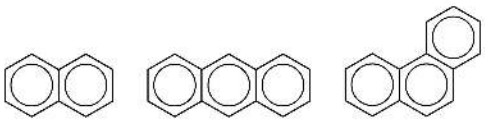

Phenyl group




2-Phenylheptane

## Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).



Naphthalene Anthracene Phenanthrene

The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

## To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

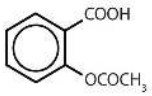
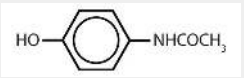
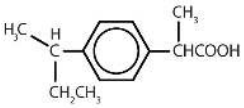
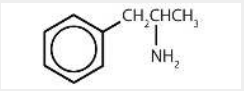
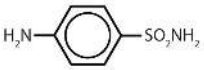
## Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they

are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, $B_2$ (riboflavin), and $B_9$ (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table **8.9.2**, also feature a benzene ring.

> So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table **8.9.2**: Some Drugs That Contain a Benzene Ring

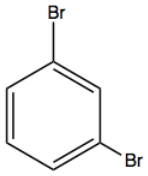
| Name | Structure |
|---|---|
| aspirin |  |
| acetaminophen |  |
| ibuprofen |  |
| amphetamine |  |
| sulfanilamide |  |

## Concept Review Exercises

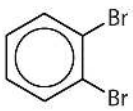
1. Briefly identify the important characteristics of an aromatic compound.
2. What is meant by the prefixes *meta*, *ortho*, or *para*? Give the name and draw the structure for a compound that illustrates each.
3. What is a phenyl group? Give the structure for 3-phenyloctane.

## Answers

1. An aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties.
2. meta = 1,3 disubstitution; (answers will vary)

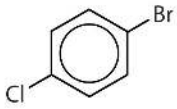


ortho = 1,2 disubstitution



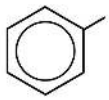
*o*-dibromobenzene or 1,2-dibromobenzene

para = 1,4 disubstitution or 1-bromo-4-chlorobenzene

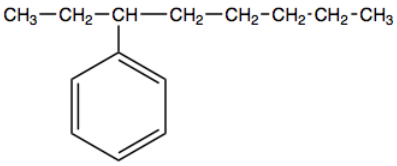



*p*-bromochlorobenzene or 1-bromo-2-chlorobenzene

3. phenyl group: $C_6H_5$ or



3-phenyloctane:

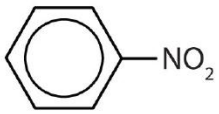


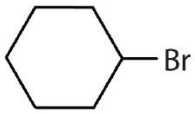

## Key Takeaway

- Aromatic compounds contain a benzene ring or have certain benzene-like properties; for our purposes, you can recognize aromatic compounds by the presence of one or more benzene rings in their structure.

## Exercises

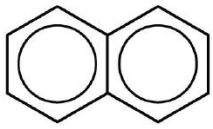
1. Is each compound aromatic?

a. 


b. 


2. Is each compound aromatic?

a. 

b. 

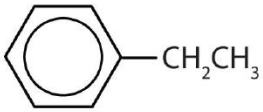
3. Draw the structure for each compound.

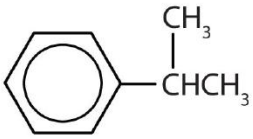
   a. toluene
   b. *m*-diethylbenzene

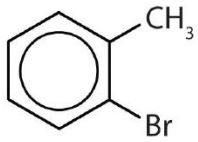
4. Draw the structure for each compound.

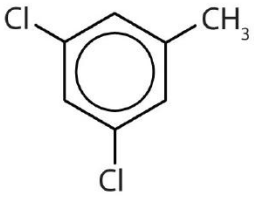
a. *p*-dichlorobenzene
b. 1,2,4-trimethylbenzene

5. Name each compound with its IUPAC name.

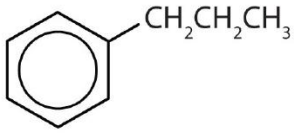
a. 

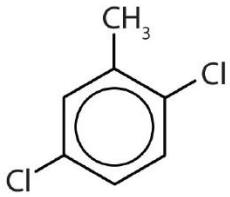

b. 

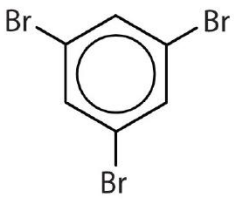

c. 


d. 


6. Name each compound with its IUPAC name.

a. 


b. 

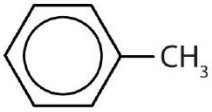

c. 

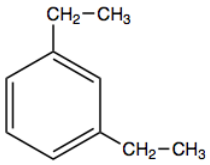

## Answers

1. a. yes
   b. no

3. a.

b.




5. a. ethylbenzene
   b. isopropylbenzene
   c. 1-bromo-2-methylbenzene or *o*-bromotoluene
   d. 1,3-dichloro-5-methylbenzene or 3,5-dichlorotoluene

---

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# 8.S: Unsaturated and Aromatic Hydrocarbons (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

Any hydrocarbon containing either a double or triple bond is an **unsaturated hydrocarbon**. **Alkenes** have a carbon-to-carbon double bond. The general formula for alkenes with one double bond is $C_nH_{2n}$. Alkenes can be straight chain, branched chain, or cyclic. Simple alkenes often have common names, but all alkenes can be named by the system of the International Union of Pure and Applied Chemistry.

**Cis-trans isomers (or geometric isomers)** are characterized by molecules that differ only in their configuration around a rigid part of the structure, such as a carbon–to-carbon double bond or a ring. The molecule having two identical (or closely related) atoms or groups on the same side is the **cis isomer**; the one having the two groups on opposite sides is the **trans isomer**.

The physical properties of alkenes are quite similar to those of alkanes. Like other hydrocarbons, alkenes are insoluble in water but soluble in organic solvents.

More reactive than alkanes, alkenes undergo **addition reactions** across the double bond:

- Addition of hydrogen (**hydrogenation**):

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$$

- Addition of halogen (**halogenation**):

$$CH_2{=}CH_2 + X_2 \rightarrow XCH_2CH_2X$$

  where X = F, Cl, Br, or I.

- Addition of water (**hydration**):

$$CH_2{=}CH_2 + HOH \rightarrow HCH_2CH_2OH$$

Alkenes also undergo **addition polymerization**, molecules joining together to form long-chain molecules.

$$\ldots CH_2{=}CH_2 + CH_2{=}CH_2 + CH_2{=}CH_2 + \ldots \rightarrow \ldots CH_2CH_2{-}CH_2CH_2{-}CH_2CH_2{-}\ldots$$

The reactant units are **monomers**, and the product is a **polymer**.

**Alkynes** have a carbon-to-carbon triple bond. The general formula for alkynes is $C_nH_{2n\,-\,2}$. The properties of alkynes are quite similar to those of alkenes. They are named much like alkenes but with the ending *-yne*.

The cyclic hydrocarbon *benzene* ($C_6H_6$) has a ring of carbon atoms. The molecule seems to be unsaturated, but it does not undergo the typical reactions expected of alkenes. The electrons that might be fixed in three double bonds are instead *delocalized* over all six carbon atoms.

A hydrocarbon containing one or more benzene rings (or other similarly stable electron arrangements) is an **aromatic hydrocarbon**, and any related substance is an **aromatic compound**. One or more of the hydrogen atoms on a benzene ring can be replaced by other atoms. When two hydrogen atoms are replaced, the product name is based on the relative position of the replacement atoms (or atom groups). A 1,2-disubstituted benzene is designated as an *ortho* (*o*-) isomer; 1,3-, a *meta* (*m*-) isomer; and 1,4-, a *para* (*p*-) isomer. A benzene ring as a substituent is called **phenyl**.

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# CHAPTER OVERVIEW

## 9: Organic Compounds of Oxygen Part 1

Ethanol and resveratrol, a phenol, are representatives of two of the families of oxygen-containing compounds that we consider in this chapter. Two other classes, aldehydes and ketones, are formed by the oxidation of alcohols. Ethers, another class, are made by the dehydration of alcohols.


9.1: Prelude to Organic Compounds of Oxygen
9.2: Organic Compounds with Functional Groups
9.3: Alcohols - Nomenclature and Classification
9.4: Physical Properties of Alcohols
9.5: Redox Reactions in Organic Chemistry and Biochemistry
9.6: Reactions that Form Alcohols
9.7: Reactions of Alcohols
9.8: Glycols and Glycerol
9.9: Phenols
9.10: Ethers
9.11: Organic Sulfur Compounds
9.S: Organic Compounds of Oxygen (Summary)


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# 9.1: Prelude to Organic Compounds of Oxygen

One of the more familiar chemical compounds on Earth is ethyl alcohol (ethanol). As the intoxicant in alcoholic beverages, ethanol is often simply called alcohol. If ethanol is diluted, as it is in wine, beer, or mixed drinks with about 1 oz of liquor, and if it is consumed in small quantities, it is relatively safe. In excess—four or more drinks in a few hours—it causes intoxication, which is characterized by a loss of coordination, nausea and vomiting, and memory blackouts.

Excessive ingestion of ethanol over a long period of time leads to cirrhosis of the liver, alteration of brain cell function, nerve damage, and strong physiological addiction. Alcoholism—an addiction to ethanol—is the most serious drug problem in the United States. Heavy drinking shortens a person's life span by contributing to diseases of the liver, the cardiovascular system, and virtually every other organ of the body.

In small quantities—one or two drinks a day—ethanol might promote health. In addition to the possible benefits of modest amounts of ethanol, a chemical in red wines, resveratrol, is thought to lower the risk of heart disease. Resveratrol, found in red grapes, is an antioxidant. It inhibits the oxidation of cholesterol and subsequent clogging of the arteries. One need not drink wine to get the benefits of resveratrol, however. It can be obtained by eating the grapes or drinking red grape juice.

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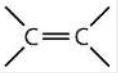
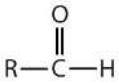
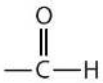
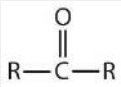
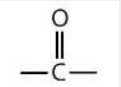
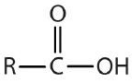
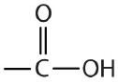
# 9.2: Organic Compounds with Functional Groups

**Learning Objectives**

- to describe functional groups and explain why they are useful in the study of organic chemistry.

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups. We first introduced the idea of the functional group, a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule. If you understand the behavior of a particular functional group, you will know a great deal about the general properties of that class of compounds. In this chapter, we make a brief yet systematic study of some of organic compound families. Each family is based on a common, simple functional group that contains an oxygen atom or a nitrogen atom. Some common functional groups are listed in Table **9.2.1**.

Table **9.2.1**: Selected Organic Functional Groups

| Name of Family | General Formula | Functional Group | Suffix* |
|---|---|---|---|
| alkane | RH | none | *-ane* |
| alkene | $R_2C{=}CR_2$ |  | *-ene* |
| alkyne | RC≡CR | –C≡C– | *-yne* |
| alcohol | ROH | –OH | *-ol* |
| thiol | RSH | –SH | *-thiol* |
| ether | ROR | –O– | ether |
| aldehyde |  |  | *-al* |
| ketone |  |  | *-one* |
| carboxylic acid |  |  | *-oic acid* |

*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

## Summary

The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.

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# 9.3: Alcohols - Nomenclature and Classification

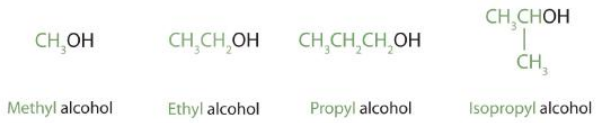
**Learning Objectives**

- Identify the general structure for an alcohol.
- Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
- Name alcohols with both common names and IUPAC names

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol ($CH_3OH$) and ethanol ($CH_3CH_2OH$) are the first two members of the homologous series of alcohols.

## Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:




Structural formula of methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol with the methyl, ethyl propyl, and isopropyl groups highlighted in green.

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

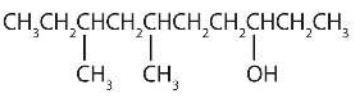
1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
2. The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the *-e* ending of the parent alkane is replaced by the suffix *-ol*. (In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
3. If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

Figure **9.3.1** shows some examples of the application of these rules.

Structures of 2 methylbutan-2-ol, 3 5-dimethylhexan-1-ol, 6 methylheptan-3-ol, 2 bromo 5 chlorocyclopentanol are shown to highlight rules 1 and 2. 1 2 ethanediol and propane 1 2 3 triol are shown to highlight rule 3
Figure **9.3.1**: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

**Example 9.3.1**

Give the IUPAC name for each compound.

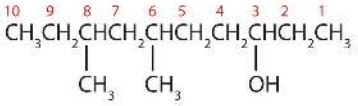
a. 


From left to right, there are ten carbon on the alkane straight chain with methyl groups emerging from carbon 3 and 5 and a hydroxyl group on carbon 8.

- $HOCH_2CH_2CH_2CH_2CH_2OH$

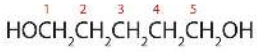
**Solution**

a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).



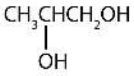
The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl ($CH_3$) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

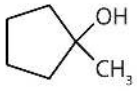
b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).



**? Exercise 9.3.1**

Give the IUPAC name for each compound.

a. 

- 

**✔ Example 9.3.2**

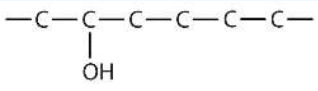
Draw the structure for each compound.

a. 2-hexanol
b. 3-methyl-2-pentanol

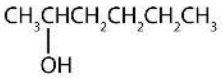
**Solution**

a. The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: –C–C–C–C–C–C–.

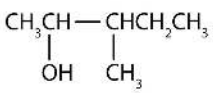
The 2 indicates that the OH group is attached to the second carbon atom.



Finally, we add enough hydrogen atoms to give each carbon atom four bonds.



- The numbers indicate that there is a methyl ($CH_3$) group on the third carbon atom and an OH group on the second carbon atom.



**? Exercise 9.3.2**

Draw the structure for each compound.

a. 3-heptanol

- 2-methyl-3-hexanol

## Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A primary (1°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is $RCH_2OH$.



- A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is $R_2CHOH$.



- A tertiary (3°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is $R_3COH$.

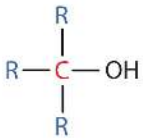
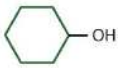


Table **9.3.1** names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:




Table **9.3.1**: Classification and Nomenclature of Some Alcohols

| Condensed Structural Formula | Class of Alcohol | Common Name | IUPAC Name |
|---|---|---|---|
| $CH_3OH$ | — | methyl alcohol | methanol |
| $CH_3CH_2OH$ | primary | ethyl alcohol | ethanol |
| $CH_3CH_2CH_2OH$ | primary | propyl alcohol | 1-propanol |
| $(CH_3)_2CHOH$ | secondary | isopropyl alcohol | 2-propanol |
| $CH_3CH_2CH_2CH_2OH$ | primary | butyl alcohol | 1-butanol |
| $CH_3CH_2CHOHCH_3$ | secondary | *sec*-butyl alcohol | 2-butanol |
| $(CH_3)_2CHCH_2OH$ | primary | isobutyl alcohol | 2-methyl-1-propanol |
| $(CH_3)_3COH$ | tertiary | *tert*-butyl alcohol | 2-methyl-2-propanol |
|  | secondary | cyclohexyl alcohol | cyclohexanol |

## Summary

In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol*. Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.

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# 9.4: Physical Properties of Alcohols

**Learning Objectives**

- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.

Alcohols can be considered derivatives of water ($H_2O$; also written as HOH).




Like the H–O–H bond in water, the R–O–H bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure **9.4.1**).

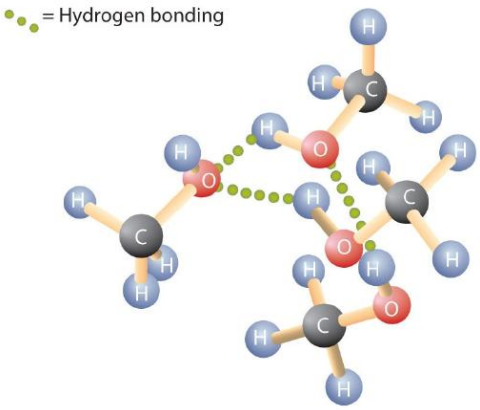



Figure **9.4.1**: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table **9.4.1** lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table **9.4.1**: Comparison of Boiling Points and Molar Masses

| Formula | Name | Molar Mass | Boiling Point (°C) |
|---|---|---|---|
| $CH_4$ | methane | 16 | –164 |
| HOH | water | 18 | 100 |
| $C_2H_6$ | ethane | 30 | –89 |
| $CH_3OH$ | methanol | 32 | 65 |
| $C_3H_8$ | propane | 44 | –42 |
| $CH_3CH_2OH$ | ethanol | 46 | 78 |
| $C_4H_{10}$ | butane | 58 | –1 |
| $CH_3CH_2CH_2OH$ | 1-propanol | 60 | 97 |

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules (Figure **9.4.2**). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.

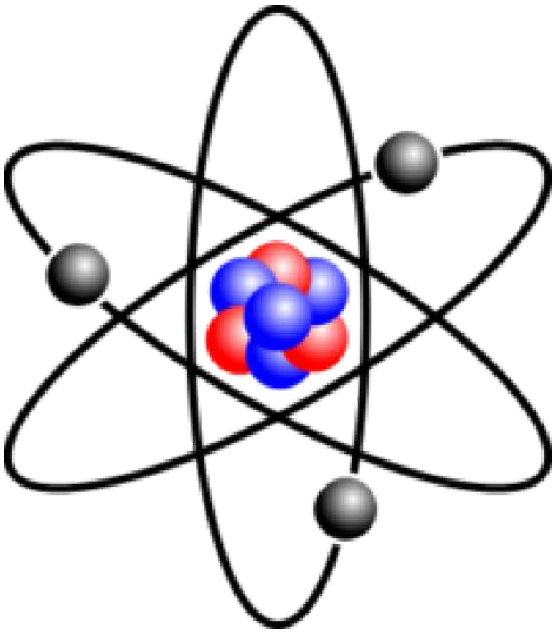


Figure **9.4.2**: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

## Summary

Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.

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# 9.5: Redox Reactions in Organic Chemistry and Biochemistry

**Learning Objectives**

- To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.



Figure **9.5.1**: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. from Wikipedia.

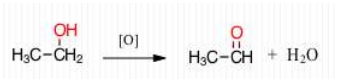
All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure **9.5.1**).

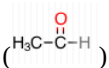
$$\mathbf{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{9.5.1}$$

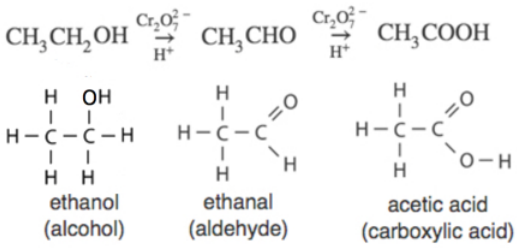
In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($\mathbf{C_6H_{12}O_6}$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:

$$\mathbf{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O} \tag{9.5.2}$$

Organic chemists use a variety of redox reactions. For example, potassium dichromate ($\mathbf{K_2Cr_2O_7}$) is a common oxidizing agent that can be used to oxidize alcohols (symbolized by the general formula ROH). The product of the reaction depends on the location of the OH functional group in the alcohol molecule, the relative proportions of alcohol and the dichromate ion, and reaction conditions such as temperature. If the OH group is attached to a terminal carbon atom and the product is distilled off as it forms, the product is an aldehyde, which has a terminal *carbonyl group* (C=O) and is often written as RCHO. One example is the reaction used by the Breathalyzer to detect ethyl alcohol ($\mathbf{CH_3CH_2OH}$) in a person's breath:

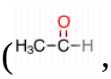



If the product acetaldehyde (  ) is not removed as it forms, it is further oxidized to acetic acid ($\mathbf{CH_3COOH}$). In this case, the overall reaction is as follows:

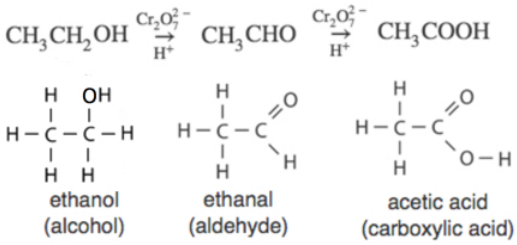


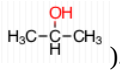
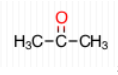


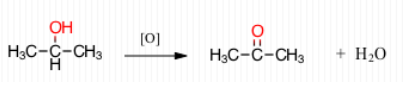
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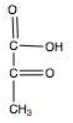
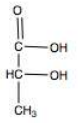
In this reaction, the chromium atom is reduced because it lost oxygen atoms from $Cr_2O_7^{2-}$ to $Cr^{3+}$. On the other hand, the carbon atom in ethanol is oxidized. In the **oxidation** of ethyl alcohol ($CH_3$-$CH_2$-OH, a.k.a. ethanol) to form acetaldehyde (  , a.k.a. ethanal), the **number of bonds to oxygen has increased and the number of hydrogen atoms has decreased** from six to four. Either or both of these indicate that an oxidation has occurred.

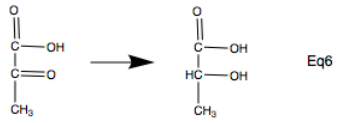
In the oxidation of acetaldehyde to acetic acid (a.k.a. ethanoic acid), the carbon atom that gained an additional oxygen is the element oxidized.




When the OH group of the alcohol is bonded to an interior carbon atom, the oxidation of an alcohol will produce a ketone (the formulas of ketones are often written as RCOR, and the carbon–oxygen bond is a double bond). The simplest ketone is derived from 2-propanol (  ). It is the common solvent acetone  , which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:



As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid,  , is reduced to lactic acid,  , in the muscles.




(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $C_6H_8O_6$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($C_6H_6O_6$). In the stomach, ascorbic acid reduces the nitrite ion ($NO_2^-$) to nitric oxide (NO):

$$C_6H_8O_6 + 2H^+ + 2NO_2^- \rightarrow C_6H_6O_6 + 2H_2O + 2NO \tag{9.5.3}$$


https://chem.libretexts.org/@go/page/288289

> *If reaction in Equation 9.5.3 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.*

Tocopherol (vitamin E) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure 9.5.2).



Figure 9.5.2: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. Wedges of pink grapefruit, lime, and lemon, and a half orange (clockwise from top). from Wikipedia.

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($C_6H_{12}O_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure 9.5.3). The overall change that occurs is as follows:

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{9.5.4}$$

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.



Figure 9.5.3: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

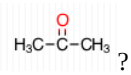
## Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

## Exercises

For the following questions, provide the answers by drawing the structures.

1. What would be the organic product if $CH_3$-$CH_2$-$CH_2$-OH were to be oxidized?
2. What would be the organic product if $CH_3$-$CH_2$-$CH_2$-$CH_2$-OH were to be oxidized?
3. What would be the organic product if 2-butanol were to be oxidized?
4. What would be the organic product if 3-pentanol were to be oxidized?

5. What alcohol (name and structure) is produced in the reduction of acetone  ?

6. What alcohol (name and structure) is produced in the reduction of propanal  ?

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# 9.6: Reactions that Form Alcohols

**Learning Objectives**

- To describe how to prepare alcohols from alkenes

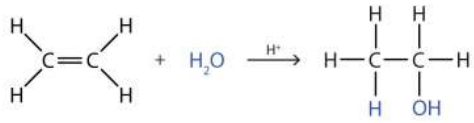
Methanol is prepared by combining hydrogen gas and carbon monoxide at high temperatures and pressures in the presence of a catalyst composed of zinc oxide (ZnO) and chromium oxide ($Cr_2O_3$) catalyst:

$$2H_2 + CO \xrightarrow[ZnO,\ Cr_2O_3]{200\ atm,\ 350°C} CH_3OH$$

Methanol is an important solvent and is used as an automotive fuel, either as the pure liquid—as in some racing cars—or as an additive in gasoline.

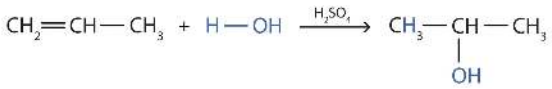
> *Nearly 2 billion gallons of methanol are produced each year in the United States by the catalytic reduction of carbon monoxide with hydrogen gas.*

Many simple alcohols are made by the hydration of alkenes. Ethanol is made by the hydration of ethylene in the presence of a catalyst such as sulfuric acid ($H_2SO_4$).



Ethylene Water Ethanol

In a similar manner, isopropyl alcohol is produced by the addition of water to propene (propylene).



Propylene Isopropyl alcohol (2-propanol)

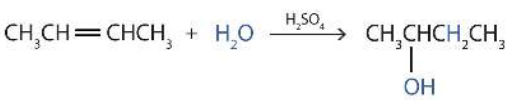
Additional Exercise **9.6.1** describes how to use a generalization called Markovnikov's rule to predict the results when the addition of water to an alcohol has two possible products.

**Example 9.6.1**

Write the equation for the reaction of 2-butene with water to form 2-butanol. Indicate that sulfuric acid is used as a catalyst.

**Solution**

First write the condensed structural formula of 2-butene and indicate that it reacts with water. Then write the condensed structural formula of 2-butanol after the reaction arrow to indicate that it is the product. Finally, write the formula for the catalyst above the arrow.



**Exercise 9.6.1**

Write the equation for the reaction of cyclopentene with water to form cyclopentanol. Indicate that phosphoric acid ($H_3PO_4$) is used as a catalyst.

> *Many OH compounds in living systems are formed by alkene hydration. Here is an example that occurs in the Krebs cycle: fumarate is hydrated to form malate.*
>
> $$^-OOCCH{=}CHCOO^- + HOH \overset{\text{enzyme}}{\rightleftharpoons} {}^-OOCCH_2CHOHCOO^-$$

In addition to its preparation from ethylene, ethanol is made by the fermentation of sugars or starch from various sources (potatoes, corn, wheat, rice, etc.). Fermentation is catalyzed by enzymes found in yeast and proceeds by an elaborate multistep mechanism. We can represent the overall process as follows:

$$(C_6H_{10}O_5)_x \xrightarrow{\text{enzymes}} C_6H_{12}O_6 \xrightarrow{\text{enzymes}} 2CH_3CH_2OH + 2CO_2$$

Starch → Glucose → Ethanol

### To Your Health: The Physiological Effects of Alcohols

Methanol is quite poisonous to humans. Ingestion of as little as 15 mL of methanol can cause blindness, and 30 mL (1 oz) can cause death. However, the usual fatal dose is 100 to 150 mL. The main reason for methanol's toxicity is that we have liver enzymes that catalyze its oxidation to formaldehyde, the simplest member of the aldehyde family:

$$CH_3OH \xrightarrow{\text{liver enzymes}} H{-}\overset{\overset{O}{\|}}{C}{-}H$$

Methanol → Formaldehyde

Formaldehyde reacts rapidly with the components of cells, coagulating proteins in much the same way that cooking coagulates an egg. This property of formaldehyde accounts for much of the toxicity of methanol.

Organic and biochemical equations are frequently written showing only the organic reactants and products. In this way, we focus attention on the organic starting material and product, rather than on balancing complicated equations.

Ethanol is oxidized in the liver to acetaldehyde:

$$CH_3CH_2OH \xrightarrow{\text{liver enzymes}} CH_3{-}\overset{\overset{O}{\|}}{C}{-}H$$

Ethanol → Acetaldehyde

The acetaldehyde is in turn oxidized to acetic acid ($HC_2H_3O_2$), a normal constituent of cells, which is then oxidized to carbon dioxide and water. Even so, ethanol is potentially toxic to humans. The rapid ingestion of 1 pt (about 500 mL) of pure ethanol would kill most people, and acute ethanol poisoning kills several hundred people each year—often those engaged in some sort of drinking contest. Ethanol freely crosses into the brain, where it depresses the respiratory control center, resulting in failure of the respiratory muscles in the lungs and hence suffocation. Ethanol is believed to act on nerve cell membranes, causing a diminution in speech, thought, cognition, and judgment.

Rubbing alcohol is usually a 70% aqueous solution of isopropyl alcohol. It has a high vapor pressure, and its rapid evaporation from the skin produces a cooling effect. It is toxic when ingested but, compared to methanol, is less readily absorbed through the skin.

## Summary

Many alcohols are made by the hydration of alkenes. Ethanol can be made by the fermentation of sugars or starch from various sources.

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# 9.7: Reactions of Alcohols

**Learning Objectives**

1. Give two major types of reactions of alcohols.
2. Describe the result of the oxidation of a primary alcohol.
3. Describe the result of the oxidation of a secondary alcohol.

Chemical reactions in alcohols occur mainly at the functional group, but some involve hydrogen atoms attached to the OH-bearing carbon atom or to an adjacent carbon atom. Of the three major kinds of alcohol reactions, which are summarized in Figure **9.7.1**, two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.

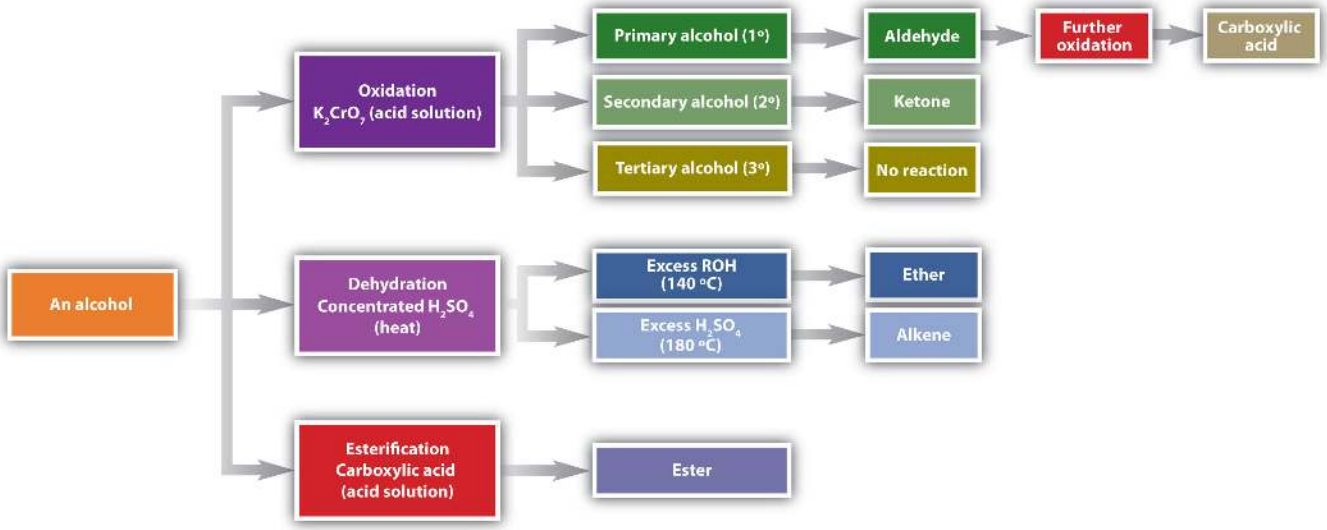
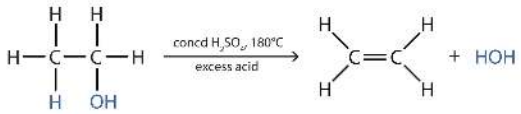



Figure **9.7.1**: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.

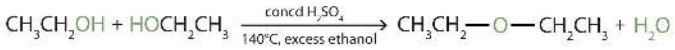
- ## Dehydration

  As noted in Figure **9.7.1**, an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule:




Ethanol Ethylene

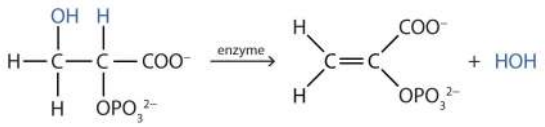
Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.




Two molecules of ethanol Diethyl ether

(Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

> Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway

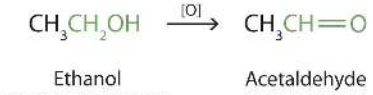



2-Phosphoglycerate Phosphoenolpyruvate

Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

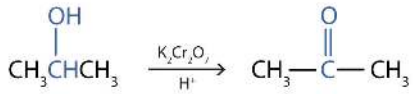
## Oxidation

Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—a primary alcohol—to form acetaldehyde—an aldehyde—as follows:




Ethanol (a primary alcohol) Acetaldehyde (an aldehyde)

We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to *ketones*. The oxidation of isopropyl alcohol by potassium dichromate ($K_2Cr_2O_7$) gives acetone, the simplest ketone:



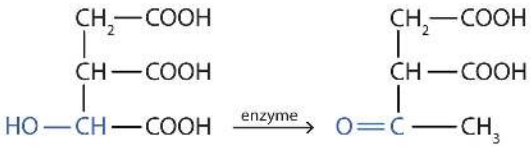

Isopropyl alcohol (a secondary alcohol) Acetone (a ketone)

Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary ($RCH_2OH$) and secondary ($R_2CHOH$) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

These reactions can also be carried out in the laboratory with chemical oxidizing agents. One such oxidizing agent is potassium dichromate. The balanced equation (showing only the species involved in the reaction) in this case is as follows:



Alcohol oxidation is important in living organisms. Enzyme-controlled oxidation reactions provide the energy cells need to do useful work. One step in the metabolism of carbohydrates involves the oxidation of the secondary alcohol group in isocitric acid to a ketone group:




Isocitrate Oxalosuccinate

The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

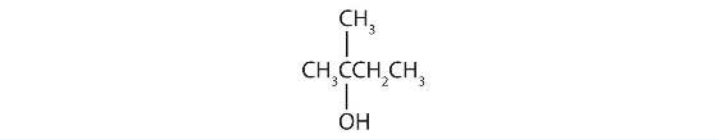
Tertiary alcohols ($R_3COH$) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the

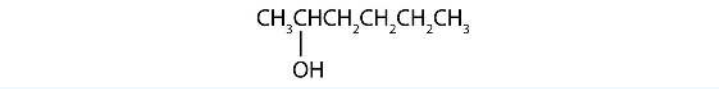
formation of a carbon-to-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-to-hydrogen bonding is easily broken under oxidative conditions, but carbon-to-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

**Example 9.7.1**

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.

a. $CH_3CH_2CH_2CH_2CH_2OH$

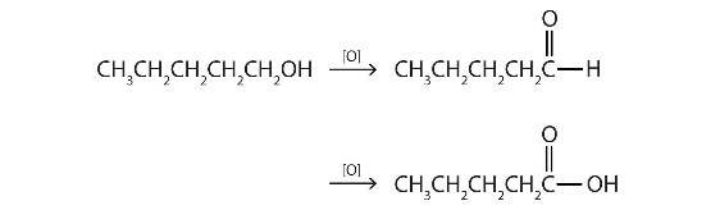
b. 

c. 

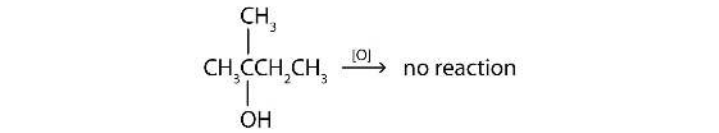
**Solution**

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

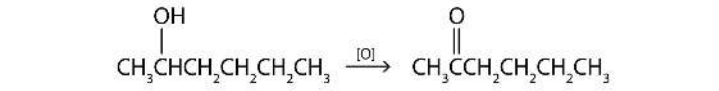
a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No reaction occurs.

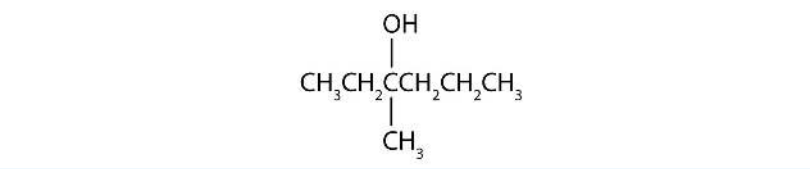


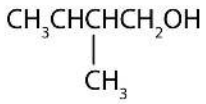
c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.

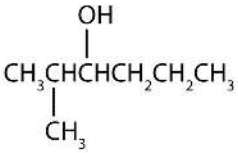


**Exercise 9.7.1**

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.

1. 

2. 

3. 

## Summary

Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

## Concept Review Exercises

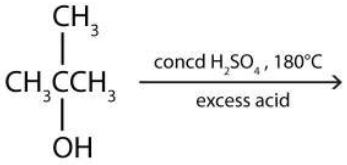
1. In a reaction, compound W with the molecular formula $C_4H_{10}O$ is converted to compound X with the formula $C_4H_8O$. Is W oxidized, reduced, dehydrated, or none of these? Explain.
2. In a reaction, 2 mol of compound Y with the molecular formula $C_4H_{10}O$ is converted to 1 mol of compound Z with the formula $C_8H_{18}O$. Is Y oxidized, reduced, or neither? Explain.

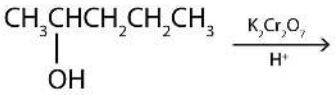
## Answers

1. oxidized; H is removed
2. neither; water is removed

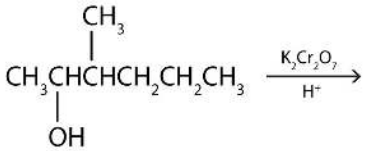
## Exercises

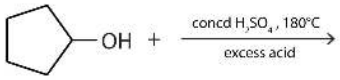
1. Name the three major types of chemical reactions of alcohols.
2. Why do tertiary alcohols not undergo oxidation? Can a tertiary alcohol undergo dehydration?
3. Draw the structure of the product for each reaction.

a. 


b. 


4. Draw the structure of the product for each reaction.

a. 

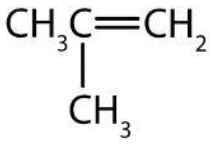

b. 

5. Draw an equation for the dehydration of 2-propanol to yield each compound type.
   a. an alkene
   b. an ether
6. Draw the structure of the alkene formed by the dehydration of cyclohexanol.

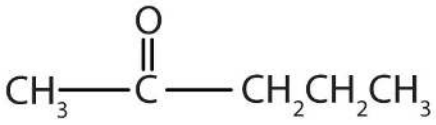
## Answers

1. dehydration, oxidation, and esterification

3. a.

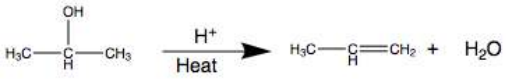


b.

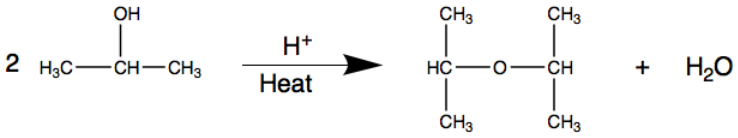


5.

a.



b.



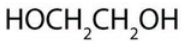
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# 9.8: Glycols and Glycerol

**Learning Objectives**

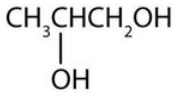
- To describe the structure and uses of some common polyhydric alcohols.

Alcohols with two OH groups on adjacent carbon atoms are commonly known as glycols. The most important of these is 1,2-ethanediol (the common name is ethylene glycol), a sweet, colorless, somewhat viscous liquid.



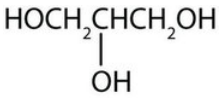
Ethylene glycol

Another common glycol, 1,2-propanediol, is commonly called propylene glycol. Its physical properties are quite similar to those of ethylene glycol.



Propylene glycol

Commonly called glycerol or glycerin, 1,2,3-propanetriol is the most important trihydroxy alcohol. Like the two glycols, it is a sweet, syrupy liquid. Glycerol is a product of the hydrolysis of fats and oils.

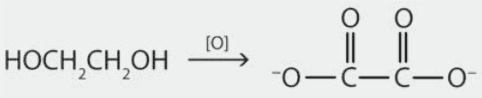


Glycerol

Ethylene glycol is the main ingredient in many antifreeze mixtures for automobile radiators. The two OH groups lead to extensive intermolecular hydrogen bonding. This results in a high boiling point—198°C; thus ethylene glycol does not boil away when it is used as an antifreeze. It is also completely miscible with water. A solution of 60% ethylene glycol in water freezes at −49°C (−56°F) and thus protects an automobile radiator down to that temperature. Ethylene glycol is also used in the manufacture of polyester fiber and magnetic film used in tapes for recorders and computers.

**To Your Health: Glycols and Human Health**

Ethylene glycol is quite toxic. Because it is sweet, pets often lap up spills of leaked antifreeze from a garage floor or driveway. Sometimes people, especially children, drink it. As with methanol, its toxicity is due to a metabolite. Liver enzymes oxidize ethylene glycol to oxalate ion.



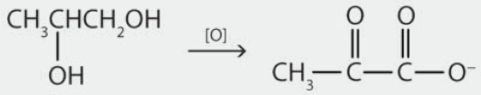
Ethylene glycol Oxalate ion

In the kidneys, the oxalate ion combines with the calcium ($Ca^{2+}$) ion, precipitating as calcium oxalate ($CaC_2O_4$).

$$Ca^{2+}(aq) + C_2O_4{}^{2-}(aq) \rightarrow CaC_2O_4(s)$$

These crystals cause renal damage and can lead to kidney failure and death.

Although propylene glycol has physical properties much like those of ethylene glycol, its physiological properties are quite different. Propylene glycol is essentially nontoxic, and it can be used as a solvent for drugs and as a moisturizing agent for foods. Like other alcohols, propylene glycol is oxidized by liver enzymes.




Propylene glycol Pyruvate ion

In this case, however, the product is pyruvate ion, a normal intermediate in carbohydrate metabolism. Glycerol, a product of fat metabolism, is essentially nontoxic.

## Summary

Glycols are alcohols with two OH groups on adjacent carbon atoms. Glycerol is the most important trihydroxy alcohol.

## Concept Review Exercises

1. In the oxidation of propylene glycol to pyruvic acid, what functional groups in the reactant are involved? What new functional groups appear in the product?
2. Oxalate ion is formed by the oxidation of ethylene glycol. In what kind of reaction is the oxalate ion involved?

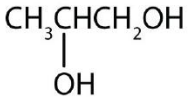
## Answers

1. two OH groups; a ketone group and a carboxylic acid group
2. precipitation

## Exercises

1. What is a glycol?
2. Why is ethylene glycol so much more toxic to humans than propylene glycol?
3. Draw the structure for each compound.
   a. 1,5-pentanediol
   b. propylene glycol
4. Draw the structure for each compound.
   a. 1,3-hexandiol
   b. glycerol

## Answers

1. an alcohol with two OH groups on adjacent carbon atoms
3. a. $HOCH_2CH_2CH_2CH_2CH_2OH$
   b. 


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# 9.9: Phenols

**Learning Objectives**

- To describe the structure and uses of some phenols

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called phenols. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.

$$\mathrm{ArOH\,(aq) + NaOH\,(aq) \rightarrow ArONa\,(aq) + H_2O}$$

The parent compound, $C_6H_5OH$, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive ("hospital smell") odor.

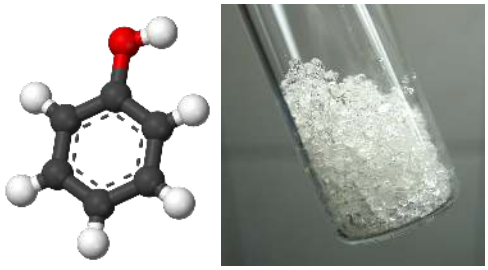


Figure 9.9.1: (Left) Structure of Phenol (right) Approximately two grams of phenol in glass vial. from Wikipedia

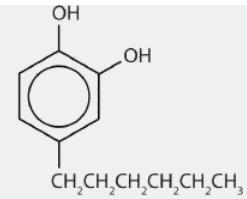
**To Your Health: Phenols and Us**

Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.



*An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.*

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring). It is much more powerful than phenol as a germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.




The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

*The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.*

## Summary

Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.

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# 9.10: Ethers

**Learning Objectives**

- Describe the structural difference between an alcohol and an ether that affects physical characteristics and reactivity of each.
- Name simple ethers.
- Describe the structure and uses of some ethers.

With the general formula R-O-R′, an ether may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups. It may also be considered a derivative of an alcohol (R-O-H) in which the hydrogen atom of the OH group is been replaced by a second alkyl or aryl group:

$$\mathrm{HOH} \xrightarrow[\text{H atoms}]{\text{replace both}} \mathrm{R-O-R'} \xleftarrow[\text{of OH group}]{\text{replace H atom}} \mathrm{R-O-H} \tag{9.10.1}$$

Simple ethers have simple common names, formed from the names of the groups attached to oxygen atom, followed by the generic name *ether*. For example, $CH_3$–O–$CH_2$-$CH_2$-$CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di-*, as in dimethyl ether ($CH_3$–O–$CH_3$) and diethyl ether $CH_3$-$CH_2$–O–$CH_2$-$CH_3$.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table **9.10.1**).

Table **9.10.1**: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

| Condensed Structural Formula | Name | Molar Mass | Boiling Point (°C) | Intermolecular Hydrogen Bonding in Pure Liquid? |
|---|---|---|---|---|
| $CH_3$-$CH_2$-$CH_3$ | propane | 44 | –42 | no |
| $CH_3$-O-$CH_3$ | dimethyl ether or methoxymethane | 46 | –25 | no |
| $CH_3$-$CH_2$-OH | ethyl alcohol or ethanol | 46 | 78 | yes |
| $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_3$ | pentane | 72 | 36 | no |
| $CH_3$-$CH_2$-O-$CH_2$-$CH_3$ | diethyl ether or ethoxy ethane | 74 | 35 | no |
| $CH_3$-$CH_2$-$CH_2$-$CH_2$-OH | butyl alcohol or 1-butanol | 74 | 117 | yes |

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula $C_2H_6O$) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

The IUPAC name for $CH_3$-O-$CH_3$ is methoxymethane and for $CH_3$–O–$CH_2$-$CH_2$-$CH_3$ is 1-methoxypropane. For $CH_3$–O–$CH_2$-$CH_2$-$CH_3$, the longer carbon chain on the right side of the oxygen is considered the base name and the shorter carbon chain on the left side of the oxygen is considered the substituent. However, since the methyl substituent is connected directly to an oxygen then the substituent name become methoxy.

## Example 9.10.1

What is the IUPAC name for each ether?

a. $CH_3$-$CH_2$-$CH_2$-O-$CH_2$-$CH_2$-$CH_3$

b. 

**Solution**

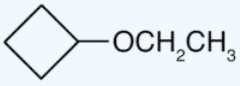
a. The carbon groups on either side of the oxygen atom are propyl ($CH_3CH_2CH_2$) groups, so the compound is propoxypropane.

b. The three-carbon group is attached by the middle carbon atom #2. The one-carbon group is a methyl group. The compound is 2-methoxypropane.

## Exercise 9.10.1

What is the IUPAC name for each ether?

a. $CH_3$-$CH_2$-$CH_2$-$CH_2$-O-$CH_2$-$CH_2$-$CH_2CH_3$

b. 

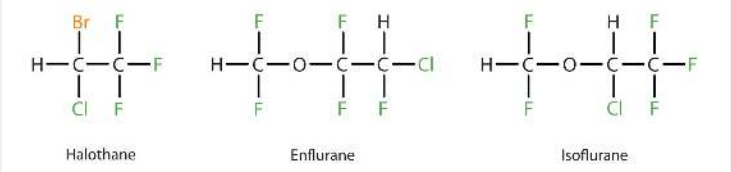
## To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.



William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



*These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.*

## Summary

To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*. Ether molecules have no OH group and thus no intermolecular hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

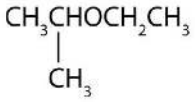
## Concept Review Exercises

1. Why does ethoxyethane ($CH_3$-$CH_2$-O-$CH_2$-$CH_3$) have a much lower boiling point than 1-butanol ($CH_3$-$CH_2$-$CH_2$-$CH_2$-OH)?
2. Which is more soluble in water—methoxyethane ($CH_3$-$CH_2$-O-$CH_3$) or 1-butanol ($CH_3$-$CH_2$-$CH_2$-$CH_2$-OH)? Explain.

## Answers

1. Diethyl ether has no intermolecular hydrogen bonding because there is no OH group; 1-butanol has an OH and engages in intermolecular hydrogen bonding.
2. Ethyl methyl ether (three carbon atoms, one oxygen atom) is more soluble in water than 1-butanol (four carbon atoms, one oxygen atom), even though both can engage in hydrogen bonding with water.

## Exercises

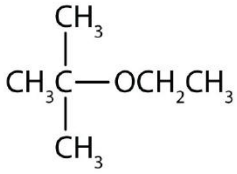
1. How can ethanol give two different products when heated with an acid catalyst? Name these products.
2. Which of these ethers is isomeric with ethanol: $CH_3$-$CH_2$-O-$CH_2$-$CH_3$, $CH_3$-O-$CH_2CH_3$, or $CH_3$-O-$CH_3$?
3. Provide the IUPAC name each compound.
   a. $CH_3$-O-$CH_2$-$CH_2$-$CH_3$
   b. 
4. Provide the IUPAC name of each compound.
   a. $CH_3$-$CH_2$-$CH_2$-$CH_2$O-$CH_3$
   b. $CH_3$-$CH_2$-O-$CH_2$-$CH_2CH_3$
5. Draw the structure for each compound.
   a. methoxypropane
   b. 2-ethoxy-2-methyl propane
6. Draw the structure for each compound.
   a. 2-isopropoxypropane
   b. propoxycyclopropane

## Answers

1. Intramolecular (both the H and the OH come from the same molecule) dehydration gives ethene; intermolecular (the H comes from one molecule and the OH comes from another molecule) dehydration gives ethoxyethane.

3. a. 1-methoxypropane
   b. 2-ethoxypropane

5. a. $CH_3$-O-$CH_2$-$CH_3$

b. 

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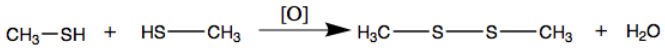
# 9.11: Organic Sulfur Compounds

**Learning Objectives**

- Identify thiols (mercaptans) by the presence of an SH group.
- The mild oxidation of thiols gives disulfides.

Because sulfur is in the same group (6A) of the periodic table as oxygen, the two elements have some similar properties. We might expect sulfur to form organic compounds related to those of oxygen, and indeed it does. Thiols (also called mercaptans), which are sulfur analogs of alcohols, have the general formula RSH. Methanethiol (also called methyl mercaptan), has the formula $CH_3SH$. Ethanethiol (ethyl mercaptan) is the most common odorant for liquid propane (LP) gas.

The mild oxidation of thiols gives compounds called disulfides.




The amino acids cysteine and methionine contain sulfur atoms, as do all proteins that contain these amino acids. Disulfide linkages (–S–S–) between protein chains are extremely important in protein structure.

Thioethers, which are sulfur analogs of ethers, have the form general formula RSR′. An example is dimethylsulfide ($CH_3SCH_3$), which is responsible for the sometimes unpleasant odor of cooking cabbage and related vegetables. Note that methionine has a thioether functional group.

**Career Focus: Paramedic**

Paramedics are highly trained experts at providing emergency medical treatment. Their critical duties often include rescue work and emergency medical procedures in a wide variety of settings, sometimes under extremely harsh and difficult conditions. Like other science-based professions, their work requires knowledge, ingenuity, and complex thinking, as well as a great deal of technical skill. The recommended courses for preparation in this field include anatomy, physiology, medical terminology, and—not surprisingly—chemistry. An understanding of basic principles of organic chemistry, for example, is useful when paramedics have to deal with such traumas as burns from fuel (hydrocarbons) or solvent (alcohols, ethers, esters, and so on) fires and alcohol and drug overdoses.

To become a paramedic requires 2–4 y of training and usually includes a stint as an emergency medical technician (EMT). An EMT provides basic care, can administer certain medications and treatments, such as oxygen for respiratory problems and epinephrine (adrenalin) for allergic reactions, and has some knowledge of common medical conditions. A paramedic, in contrast, must have extensive knowledge of common medical problems and be trained to administer a wide variety of emergency drugs.

Paramedics usually work under the direction of a medical doctor with a title such as “medical director.” Some paramedics are employed by fire departments and may work from a fire engine that carries medical equipment as well as fire-fighting gear. Some work from hospital-sponsored ambulances and continue to care for their patients after reaching the hospital emergency room. Still other paramedics work for a government department responsible for emergency health care in a specific geographical area. Finally, some work for private companies that contract to provide service for a government body.

An experienced paramedic has a broad range of employment options, including training for mountain or ocean rescue, working with police department special weapons and tactics (SWAT) teams, or working in isolated settings such as on oil rigs. With their expertise at treating and stabilizing patients before quickly moving them to a hospital, paramedics often provide the first critical steps in saving an endangered life. The following quotation, inscribed on the Arlington National Cemetery headstone of Army Lieutenant R. Adams Cowley, who is often called the “father” of shock trauma medicine, serves as the motto for many paramedic units: “Next to creating a life the finest thing a man can do is save one.” —Abraham Lincoln

## Summary

Thiols, thioethers, and disulfides are common in biological compounds.

## Concept Review Exercises

1. What is the functional group of a thiol? Write the condensed structural formula for ethanethiol (ethyl mercaptan).
2. What is the functional group of a disulfide? Write the condensed structural formula for dipropyl disulfide.

## Answers

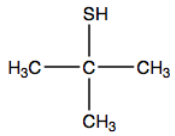
1. SH; $CH_3CH_2SH$
2. –S–S–; $CH_3$-$CH_2$-$CH_2$-S-S-$CH_2$-$CH_2$-$CH_3$

## Exercises

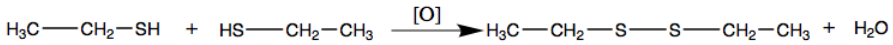
1. A common natural gas odorant is 2-methyl-2-propanethiol. What is its condensed structural formula?
2. Write the equation for the oxidation of ethanethiol to diethyl disulfide.

## Answer

1.




2.




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# 9.S: Organic Compounds of Oxygen (Summary)

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# CHAPTER OVERVIEW

## 10: Organic Compounds of Oxygen Part 2


10.1: Aldehydes and Ketones- Structure and Names

10.2: Properties of Aldehydes and Ketones

10.3: Addition Reactions for Aldehydes and Ketones


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# 10.1: Aldehydes and Ketones- Structure and Names

**Learning Objectives**

- Identify the general structure for an aldehyde and a ketone.
- Use common names to name aldehydes and ketones.
- Use the IUPAC system to name aldehydes and ketones.

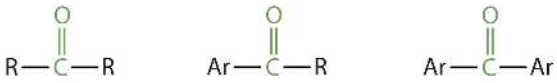
The next functional group we consider, the carbonyl group, has a carbon-to-oxygen double bond.



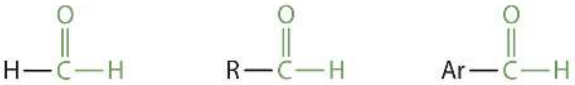
Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones.

> *The carbonyl group is ubiquitous in biological compounds. It is found in carbohydrates, fats, proteins, nucleic acids, hormones, and vitamins—organic compounds critical to living systems.*

In a ketone, two carbon groups are attached to the carbonyl carbon atom. The following general formulas, in which R represents an alkyl group and Ar stands for an aryl group, represent ketones.

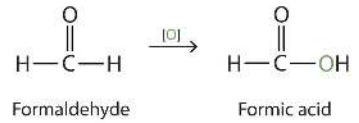


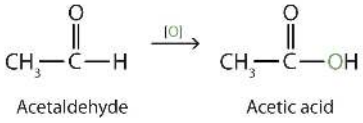

In an aldehyde, at least one of the attached groups must be a hydrogen atom. The following compounds are aldehydes:




- ## Naming Aldehydes and Ketones

  Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.

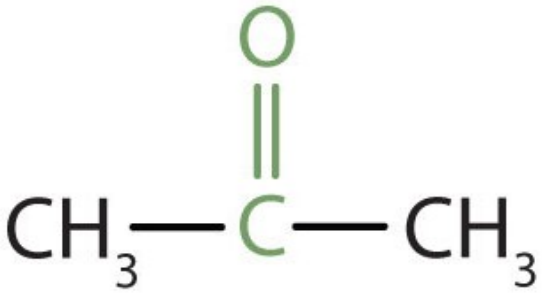



- The stems for the common names of the first four aldehydes are as follows:

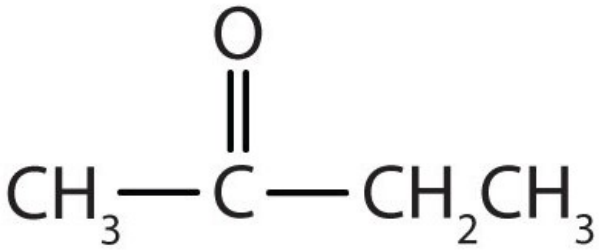
  - 1 carbon atom: *form-*
  - 2 carbon atoms: *acet-*
  - 3 carbon atoms: *propion-*
  - 4 carbon atoms: *butyr-*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.



Acetone

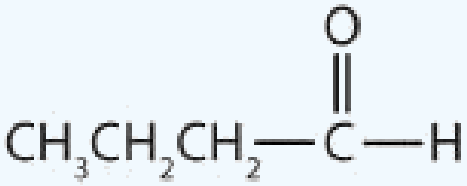
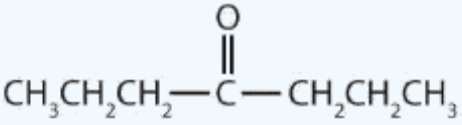
Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.

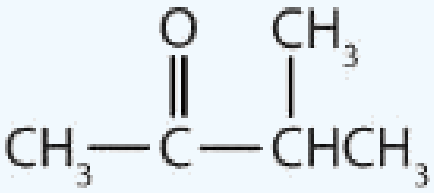


Ethyl methyl ketone

**Example 10.1.1**

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

1. 
2. 

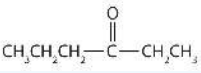
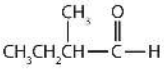
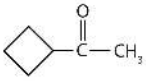
3. 

**Solution**

1. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.
2. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.
3. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

**Exercise 10.1.1**

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

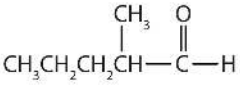
1. 
2. 
3. 

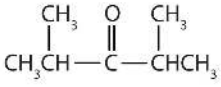
Here are some simple IUPAC rules for naming aldehydes and ketones:

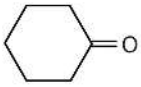
1. The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
2. For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
3. For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
4. To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
5. To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

**Example 10.1.2**

Give the IUPAC name for each compound.

a. 

b. 

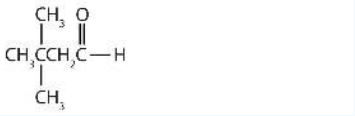
c. 

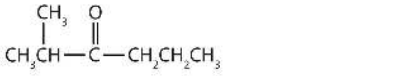
**Solution**

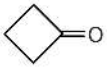
a. There are five carbon atoms in the LCC. The methyl group ($CH_3$) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.
b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.
c. There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

## Exercise

Give the IUPAC name for each compound.

a. 

b. 

c. 

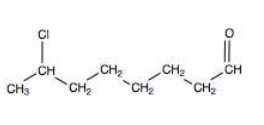
## Example 10.1.3

Draw the structure for each compound.

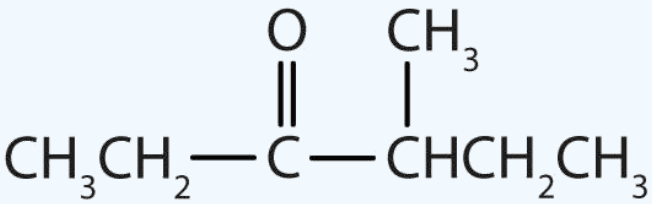
a. 7-chlorooctanal
b. 4-methyl–3-hexanone

**Solution**

a. The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.



b. The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl ($CH_3$) group at C4:



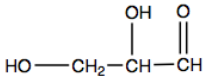
**Exercise**

Draw the structure for each compound.

a. 5-bromo-3-iodoheptanal
b. 5-bromo-4-ethyl-2-heptanone

## Concept Review Exercises

1. Give the structure and IUPAC name for the compound that has the common name *m*-bromobenzaldehyde.



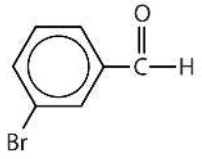

2. Give the IUPAC name for glyceraldehyde, . So here is where we have two functional groups on the same molecule. Aldehydes take priority over -OH groups. Thus, we keep the suffix -al, but use hydroxy to name the alcohol as the lower priority substituent.

   (Hint: as a substituent, the OH group is named *hydroxy*.)

## Summary

The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

## Answers

1. 

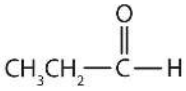

   3-Bromobenzaldehyde

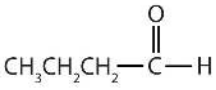
   3-bromobenzaldehyde

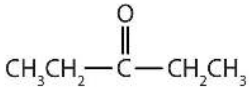
2. 2,3-dihydroxypropanal

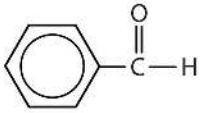
## Exercises

1. Name each compound by IUPAC nomenclature.

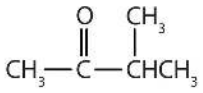
   a. 

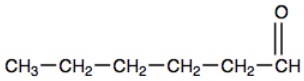

   b. 

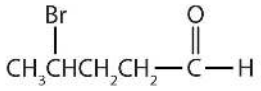

   c. 

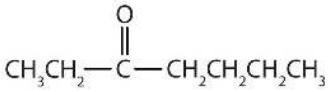

   d. 

2. Name each compound by IUPAC nomenclature.

a. 

b. 

c. 

d. 

3. Draw the structure for each compound.

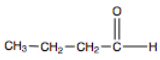
a. butanal
b. 2-hexanone
c. *p*-chlorobenzaldehyde

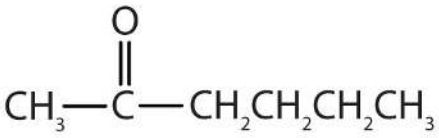
4. Draw the structure for each compound.

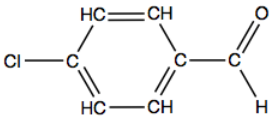
a. 5-ethyloctanal
b. 2-chloropropanal
c. 2-hydroxy-3-pentanone

## Answers

1. a. propanal
   b. butanal
   c. 3-pentanone
   d. benzaldehyde

3. a. 

b. 

c. 

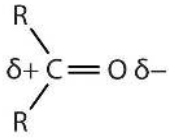
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# 10.2: Properties of Aldehydes and Ketones

**Learning Objectives**

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Name the typical reactions take place with aldehydes and ketones.
- Describe some of the uses of common aldehydes and ketones.

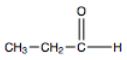
The carbon-to-oxygen double bond is quite polar, more polar than a carbon-to-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge:




In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table **10.2.1** shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

Table **10.2.1**: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

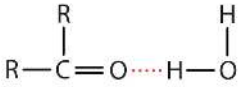
| Compound | Family | Type of Intermolecular Forces |
| --- | --- | --- |
| $CH_3CH_2CH_2CH_3$ | alkane | dispersion only |
| $CH_3OCH_2CH_3$ | ether | weak dipole |

| | | |
|---|---|---|
|  | aldehyde | strong polar |
| $CH_3CH_2CH_2OH$ | alcohol | hydrogen bonding |

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

> Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

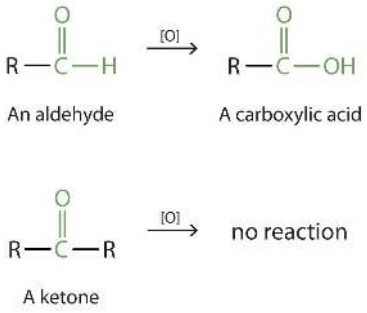
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.



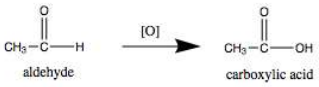
The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

- ## Oxidation of Aldehydes and Ketones

  Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.



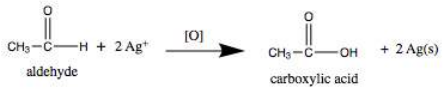

The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen ($O_2$) in air to carboxylic acids.




The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. Tollens' reagent, for example, is an alkaline solution of silver ($Ag^+$) ion complexed with ammonia ($NH_3$), which keeps the $Ag^+$ ion in solution.

$$H_3N—Ag^+—NH_3 \tag{10.2.1}$$

When Tollens' reagent oxidizes an aldehyde, the $Ag^+$ ion is reduced to free silver (Ag).

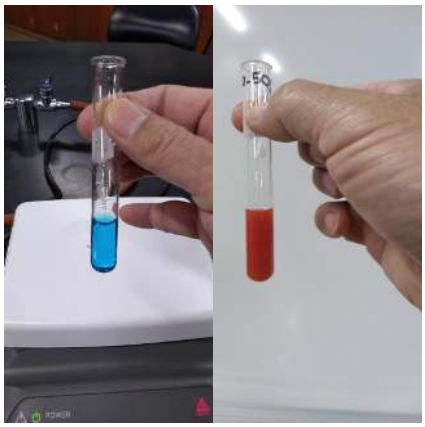



Deposited on a clean glass surface, the silver produces a mirror (Figure 10.2.1). Ordinary ketones do not react with Tollens' reagent.

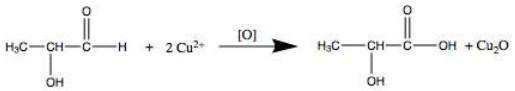


Figure 10.2.1: Aldehyde Reactions. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. Source: Photo courtesy of Krebs Glas Lauscha, commons.wikimedia.org/wiki/File:Silvering.jpg.

Another reagent named Benedict's reagent, also oxidizes aldehydes especially if there is an alcohol on the adjacent carbon next to the aldehyde functional group. Benedict's reagent contains $Cu^{2+}$ ions (blue color in aqueous solutions) which upon oxidizing the aldehyde the $Cu^{2+}$will be reduced to a $Cu^{1+}$ ion and form $Cu_2O$ (reddish brown color).



Benedict's solution (blue) and Benedict's solution mixed with glucose (red).



Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

- ## Reduction of Aldehydes and Ketones

Aldehydes and ketones can be reduced by adding hydrogen gas with a metal catalyst (i.e. Ni, Pt or Pd). Reduction of aldehydes produces primary alcohols and reduction of ketones produces secondary alcohols.

- ## Some Common Carbonyl Compounds

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms.

> *The odor of green leaves is due in part to a carbonyl compound, cis-3-hexenal, which with related compounds is used to impart a "green" herbal odor to shampoos and other products.*

Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure **10.2.2**).

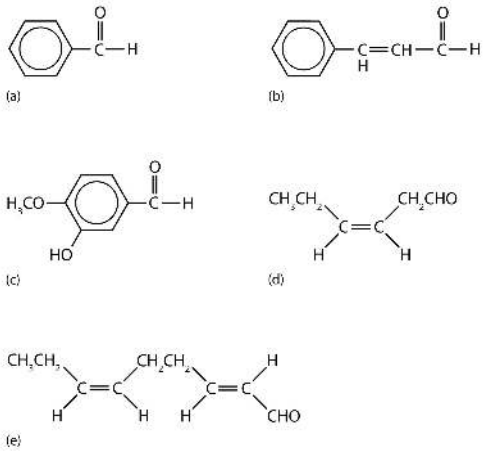


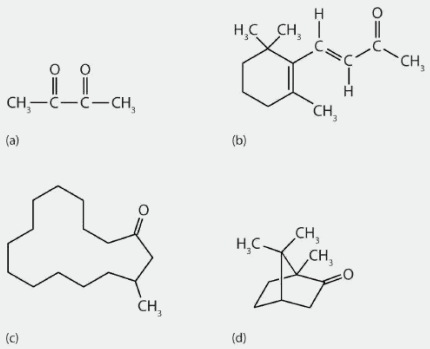
Figure **10.2.2** Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

Acetone is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail polish remover.

### To Your Health: Acetone in Blood, Urine, and Breath

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.



*Some ketones have interesting properties: (a) Butter flavoring comes from 2,3-butanedione; (b) β-ionone is responsible for the odor of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents.*

Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone, a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone, the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

## Summary

The polar carbon-to-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols that engage in intermolecular hydrogen bonding. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.

## Concept Review Exercises

1. What feature of their structure makes aldehydes easier to oxidize than ketones?
2. How does the carbon-to-oxygen bond of aldehydes and ketones differ from the carbon-to-carbon bond of alkenes?

### Answers

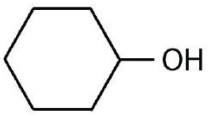
1. the H on the carbonyl carbon atom
2. The carbon-to-oxygen double bond is polar; the carbon-to-carbon double bond is nonpolar.

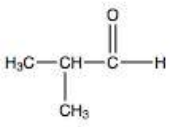
## Exercises

1. Which compound in each pair has the higher boiling point?
   a. propanone or 2-propanol
   b. methoxymethane or ethanal
2. Which compound in each pair has the higher boiling point?
   a. butanal or 1-butanol
   b. acetone (propanone) or 2-methylpropane
3. Draw the structure of the alcohol that could be oxidized to each compound.
   a. cyclohexanone
   b. 2-methylpropanal
4. Draw the structure of the alcohol that could be oxidized to each compound.
   a. 2-pentanone
   b. *o*-methylbenzaldehyde
5. Ethanal is treated with each substance.
   a. $Ag^+(aq)$—What organic product, if any, is formed?
   b. [O]—What organic product, if any, is formed?
6. Acetone (propanone) is treated with each substance.
   a. $Ag^+(aq)$ —What organic product, if any, is formed?
   b. [O] in an acid solution—What organic product, if any, is formed?

## Answers

1. a. 2-propanol
   b. ethanal

3. a. 


3. b. 


5. a. silver metal (Ag)
   b. ethanoic acid ( 

 )

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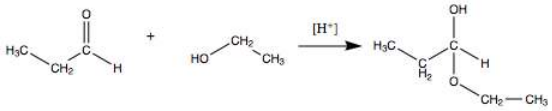
# 10.3: Addition Reactions for Aldehydes and Ketones

**Learning Objectives**

- To draw reactions consisting of alcohols with aldehyds or ketones.

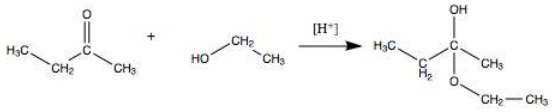
An alcohol can be added to an aldehyde with an acid catalyst to form an hemiacetal.

Reaction a:



If an alcohol is added to a ketone with an acid catalyst, a hemiketal will be produced.

Reaction b:

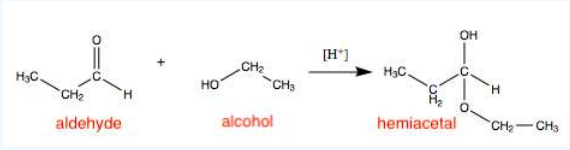


**Exercise 10.3.1**

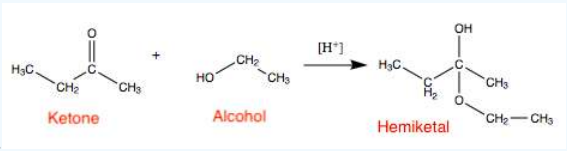
1. Redraw the above reactions and label the reactant aldehyde, ketone, and alcohol. Label the hemiacetal and hemiketal products.

## Answer

1.a.

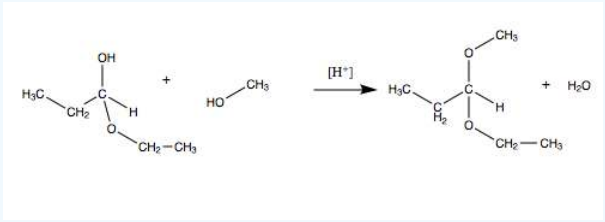



b.

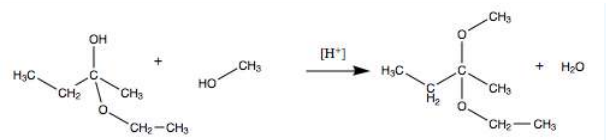



The addition of another alcohol to the hemiacetal or hemiketal will produce the acetal or ketal, respectively, along with the formation of water.

Reaction c:



Reaction d:

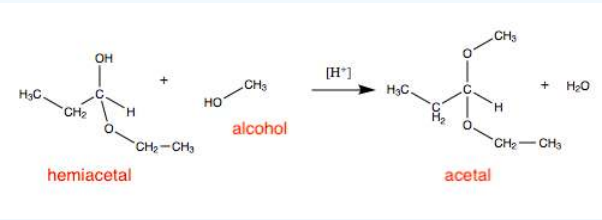


## Exercise 10.3.2

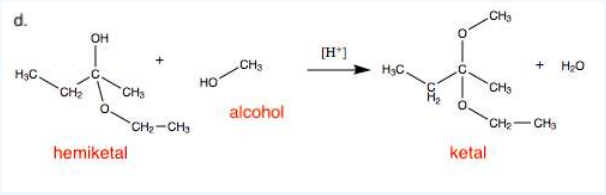
Redraw the above two reactions (c & d) and label the reactant hemiacetal, hemiketal, and alcohol. Label the acetal and ketal product.

**Answer**

c.




d.




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# CHAPTER OVERVIEW

## 11: Organic Acids and Some of Their Derivatives Part 1

Organic acids have been known for ages. Prehistoric people likely made acetic acid when their fermentation reactions went awry and produced vinegar instead of wine. The Sumerians (2900–1800 BCE) used vinegar as a condiment, a preservative, an antibiotic, and a detergent. Citric acid was discovered by an Islamic alchemist, Jabir Ibn Hayyan (also known as Geber), in the 8th century, and crystalline citric acid was first isolated from lemon juice in 1784 by the Swedish chemist Carl Wilhelm Scheele. Medieval scholars in Europe were aware that the crisp, tart flavor of citrus fruits is caused by citric acid. Naturalists of the 17th century knew that the sting of a red ant's bite was due to an organic acid that the ant injected into the wound. The acetic acid of vinegar, the formic acid of red ants, and the citric acid of fruits all belong to the same family of compounds—carboxylic acids. Soaps are salts of long-chain carboxylic acids. Prehistoric people also knew about organic bases—by smell if not by name; amines are the organic bases produced when animal tissue decays. The organic compounds that we consider in this chapter are organic acids and bases. We will also consider two derivatives of carboxylic acids: esters and amides. An ester is derived from a carboxylic acid and an alcohol. Fats and oils are esters, as are many important fragrances and flavors. An amide is derived from a carboxylic acid and either ammonia or an amine. Proteins, often called "the stuff of life," are polyamides.


11.1: Prelude to Organic Acids and Bases and Some of Their Derivatives
11.2: Carboxylic Acids - Structures and Names
11.3: The Formation of Carboxylic Acids
11.4: Physical Properties of Carboxylic Acids
11.5: Chemical Properties of Carboxylic Acids- Ionization and Neutralization
11.6: Esters - Structures and Names
11.7: Physical Properties of Esters
11.8: Preparation of Esters
11.9: Hydrolysis of Esters
11.10: Esters of Phosphoric Acid


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# 11.1: Prelude to Organic Acids and Bases and Some of Their Derivatives

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Prehistoric people also knew about organic bases—by smell if not by name; amines are the organic bases produced when animal tissue decays.

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# 11.2: Carboxylic Acids - Structures and Names

**Learning Objectives**

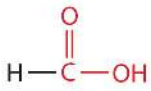
- Name carboxylic acids with common names.
- Name carboxylic acids according to IUPAC nomenclature.

Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure **11.2.1**). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



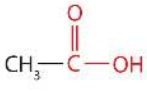

Figure **11.2.1**: Carboxylic Acids in the Home. Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock

The simplest carboxylic acid, formic acid (HCOOH), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).



Formic acid

The next higher homolog is acetic acid, which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Acetic acid

Pure acetic acid solidifies at 16.6°C, only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often “froze” on the storage shelf. For that

reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid ($CH_3CH_2COOH$), is seldom encountered in everyday life. The fourth homolog, butyric acid ($CH_3CH_2CH_2COOH$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives. Models of the first four carboxylic acids are shown in Figure **11.2.2**.

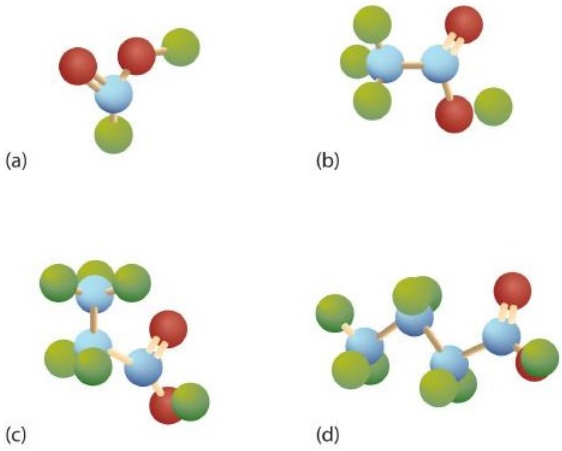
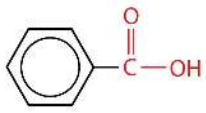


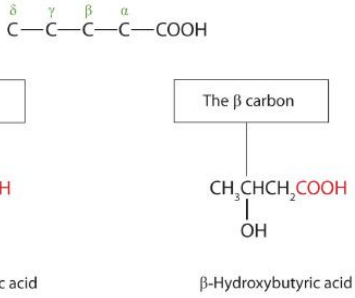

Figure **11.2.2**: Ball-and-Stick Models of Carboxylic Acids. Carboxylic acids feature a carbon atom doubly bonded to an oxygen atom and also joined to an OH group. The four acids illustrated here are formic acid (a), acetic acid (b), propionic acid (c), and butyric acid (d).

The acid with the carboxyl group attached directly to a benzene ring is called benzoic acid ($C_6H_5COOH$).




Benzoic acid

The common names of carboxylic acids use Greek letters (α, β, γ, δ, and so forth), not numbers, to designate the position of substituent groups in acids. These letters refer to the position of the carbon atom in relation to the carboxyl carbon atom.




α-Methylpropionic acid

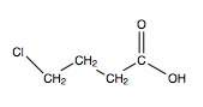
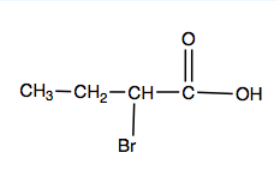
β-Hydroxybutyric acid

In the nomenclature system of the International Union of Pure and Applied Chemistry (IUPAC), the parent hydrocarbon is the one that corresponds to the longest continuous chain (LCC) containing the carboxyl group. The *-e* ending of the parent alkane is replaced by the suffix *-oic* and the word *acid*. For example, the carboxylic acid derived from pentane is pentanoic acid ($CH_3CH_2CH_2CH_2COOH$). As with aldehydes, the carboxyl carbon atom is counted first; numbers are used to indicate any substituted carbon atoms in the parent chain.

Greek letters are used with common names; numbers are used with IUPAC names.

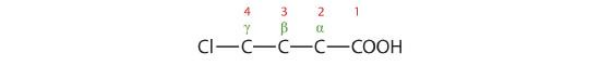
## Example 11.2.1

Give the common and IUPAC names for each compound.

1. 
2. 

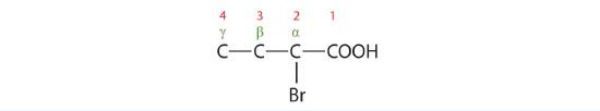
**Solution**

1. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The chlorine atom is attached to the γ-carbon in the common system or C4 in the IUPAC system. The compound is γ-chlorobutyric acid or 4-chlorobutanoic acid.

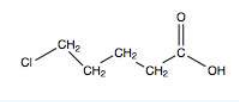
2. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.

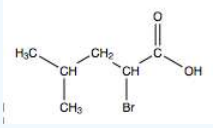


The bromine (Br) atom is at the α-carbon in the common system or C2 in the IUPAC system. The compound is α-bromobutyric acid or 2-bromobutanoic acid.

## Exercise 11.2.1

Give the IUPAC name for each compound.

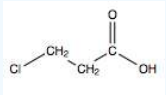
a. 

b. 

## Example 11.2.2

Write the condensed structural formula for β-chloropropionic acid.

**Solution**

Propionic acid has three carbon atoms: C–C–COOH. Attach a chlorine (Cl) atom to the parent chain at the beta carbon atom, the second one from the carboxyl group: Cl–C–C–COOH. Then add enough hydrogen atoms to give each carbon atom four bonds:  .

**Exercise 11.2.2**

Write the condensed structural formula for 4-bromo-5-methylhexanoic acid.

## Concept Review Exercises

1. What is the IUPAC name for the straight-chain carboxylic acid with six carbon atoms?
2. The straight-chain aldehyde with five carbon atoms has the common name valeraldehyde. What is the common name of the corresponding straight-chain carboxylic acid?

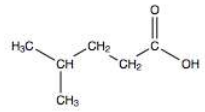
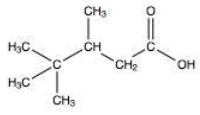
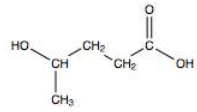
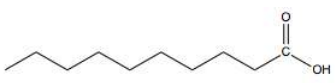
## Answers

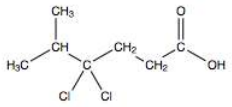
1. hexanoic acid
2. valeric acid

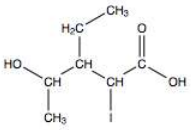
## Key Takeaways

- Simple carboxylic acids are best known by common names based on Latin and Greek words that describe their source (e.g., formic acid, Latin *formica*, meaning “ant”).
- Greek letters, not numbers, designate the position of substituted acids in the common naming convention.
- IUPAC names are derived from the LCC of the parent hydrocarbon with the *-e* ending of the parent alkane replaced by the suffix *-oic* and the word *acid*.

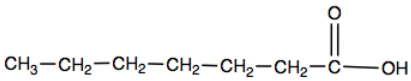
## Exercises

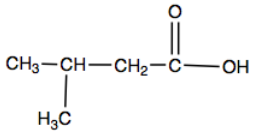
1. Draw the structure for each compound.
    a. heptanoic acid
    b. 3-methylbutanoic acid
    c. 2,3-dibromobenzoic acid
    d. β-hydroxybutyric acid
2. Draw the structure for each compound.
    a. *o*-aminobenzoic acid
    b. *p*-chlorobenzoic acid
    c. 3-chloropentanoic acid
    d. α-chloropropionic acid
3. Name each compound with the IUPAC name.
    a. 
    b. 
    c. 
4. Name each compound with its IUPAC name.
    a. 

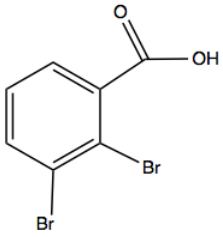
b. 

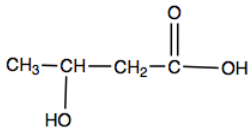
c. 

## Answers

1. a. 

b. 

c. 

d. 

3. a. 3-methylbutanoic acid
   b. 3,4,4-trimethylpentanoic acid
   c. 4-hydroxybutanoic acid

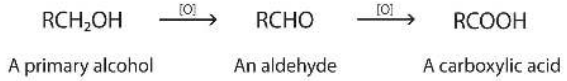
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# 11.3: The Formation of Carboxylic Acids

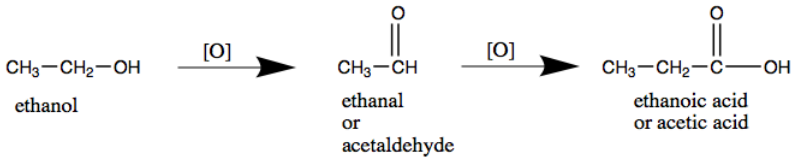
**Learning Objectives**

- To describe the preparation of carboxylic acids.

As we noted previously, the oxidation of aldehydes or primary alcohols forms carboxylic acids:




In the presence of an oxidizing agent, ethanol is oxidized to acetaldehyde, which is then oxidized to acetic acid.




This process also occurs in the liver, where enzymes catalyze the oxidation of ethanol to acetic acid.

$$\mathrm{CH_3CH_2OH} \xrightarrow[\text{oxidizing agent}]{\text{alcohol dehydrogenase}} \mathrm{CH_3CHO} \xrightarrow[\text{oxidizing agent}]{\text{alcohol dehydrogenase}} \mathrm{CH_3COOH} \tag{11.3.1}$$

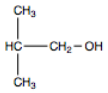
Acetic acid can be further oxidized to carbon dioxide and water.

## Summary

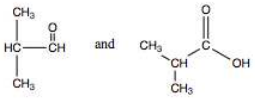
Whether in the laboratory or in the body, the oxidation of aldehydes or primary alcohols forms carboxylic acids.

## Concept Review Exercises

1. Caproic acid (hexanoic acid) can be prepared in an oxidation reaction from
   a. what alcohol?
   b. what aldehyde?

1. Give the structures of the aldehyde and the carboxylic acid formed by the oxidation of isobutyl alcohol  .

### Answers

1. a. $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-OH b. 

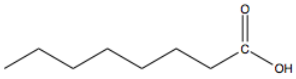
## Exercises

1. Caprylic acid (octanoic acid) can be prepared in an oxidation reaction from
   a. what alcohol?
   b. what aldehyde?
2. Give the structures of the aldehyde and the carboxylic acid formed by the oxidation of

   1,4-butanediol (HO-$CH_2$-$CH_2$-$CH_2$-$CH_2$-OH).

## Answer

1. a. $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-OH

   b. 


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# 11.4: Physical Properties of Carboxylic Acids

**Learning Objectives**

- Compare the boiling points of carboxylic acids with alcohols of similar molar mass.
- Compare the solubilities of carboxylic acids in water with the solubilities of comparable alkanes and alcohols in water.

Many carboxylic acids are colorless liquids with disagreeable odors. The carboxylic acids with 5 to 10 carbon atoms all have "goaty" odors (explaining the odor of Limburger cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated locker rooms. The acids with more than 10 carbon atoms are waxlike solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility.

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass.

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure **11.4.1**). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid [$CH_3(CH_2)_4COOH$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$CH_3(CH_2)_{14}COOH$], with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

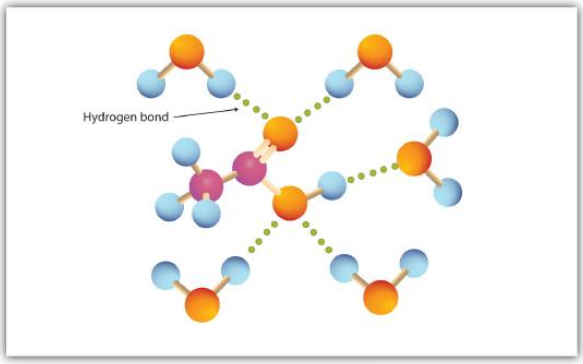



Figure **11.4.1**: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table 15.4.1 lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

Table **11.4.1**: Physical Constants of Carboxylic Acids

| Condensed Structural Formula | Name of Acid | Melting Point (°C) | Boiling Point (°C) | Solubility (g/100 g of Water) |
|---|---|---|---|---|
| HCOOH | formic acid | 8 | 100 | miscible |
| $CH_3COOH$ | acetic acid | 17 | 118 | miscible |
| $CH_3CH_2COOH$ | propionic acid | –22 | 141 | miscible |
| $CH_3(CH_2)_2COOH$ | butyric acid | –5 | 163 | miscible |
| $CH_3(CH_2)_3COOH$ | valeric acid | –35 | 187 | 5 |
| $CH_3(CH_2)_4COOH$ | caproic acid | –3 | 205 | 1.1 |
| $C_6H_5COOH$ | benzoic acid | 122 | 249 | 0.29 |

## Concept Review Exercises

1. Which compound has the higher boiling point—butanoic acid (molar mass 88) or 2-pentanone (molar mass 86)? Explain.
2. Would you expect butyric acid (butanoic acid) to be more or less soluble than 1-butanol in water? Explain.

## Answers

1. butanoic acid because of hydrogen bonding (There is no intermolecular hydrogen bonding in 2-pentanone.)
2. more soluble because there is more extensive hydrogen bonding

## Key Takeaways

- Carboxylic acids have high boiling points compared to other substances of comparable molar mass. Boiling points increase with molar mass.
- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

## Exercises

1. Which compound has the higher boiling point—$CH_3CH_2$-O-$CH_2CH_3$ or $CH_3CH_2CH_2COOH$? Explain.
2. Which compound has the higher boiling point—$CH_3CH_2CH_2CH_2OH$ or $CH_3CH_2CH_2COOH$? Explain.
3. Which compound is more soluble in water—$CH_3COOH$ or $CH_3CH_2CH_2CH_3$? Explain.
4. Which compound is more soluble in water—$CH_3CH_2COOH$ or $CH_3CH_2CH_2CH_2CH_2COOH$? Explain.

## Answers

1. $CH_3CH_2CH_2COOH$ because of hydrogen bonding (There is no intermolecular hydrogen bonding with $CH_3CH_2$-O-$CH_2CH_3$.)

3. $CH_3COOH$ because it engages in hydrogen bonding with water (There is no intermolecular hydrogen bonding with $CH_3CH_2CH_2CH_3$.)

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# 11.5: Chemical Properties of Carboxylic Acids- Ionization and Neutralization

**Learning Objectives**

- Name the typical reactions that take place with carboxylic acids.
- Describe how carboxylic acids react with basic compounds.

Water-soluble carboxylic acids ionize slightly in water to form moderately acidic solutions.

$$\mathbf{RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+}$$

Their aqueous solutions exhibit the typical properties of acids, such as changing litmus from blue to red.

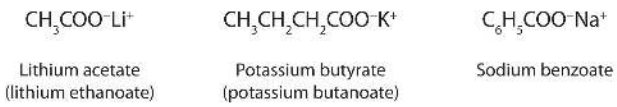
The anion formed when a carboxylic acid dissociates is called the *carboxylate* anion ($RCOO^-$).

Whether soluble in water or not, carboxylic acids react with aqueous solutions of sodium hydroxide (NaOH) to form salts:

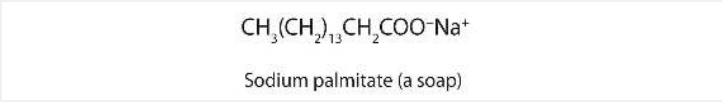
$$RCOOH + NaOH(aq) \rightarrow RCOO^-Na^+(aq) + H_2O$$

In these reactions, the carboxylic acids act like inorganic acids: they neutralize basic compounds.

Carboxylic acid salts are named in the same manner as inorganic salts: the name of the cation is followed by the name of the organic anion. The name of the anion is obtained by dropping the *-ic* ending of the acid name and replacing it with the suffix *-ate*. This rule applies whether we are using common names or International Union of Pure and Applied Chemistry (IUPAC) names:




The salts of long-chain carboxylic acids are called soaps. We discuss the chemistry of soaps elsewhere.




**Example 11.5.1**

Write an equation for each reaction.

1. the ionization of propionic acid in water ($H_2O$)
2. the neutralization of propionic acid with aqueous sodium hydroxide (NaOH)

**Solution**

Propionic acid has three carbon atoms, so its formula is $CH_3CH_2COOH$.

1. Propionic acid ionizes in water to form a propionate ion and a hydronium ($H_3O^+$) ion. $CH_3CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$
2. Propionic acid reacts with NaOH(aq) to form sodium propionate and water. $CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2COO^-Na^+(aq) + H_2O(\ell)$

**Exercise 11.5.1**

Write an equation for each reaction.

a. the ionization of formic (methanoic acid) acid in water
b. the ionization of *p*-chlorobenzoic acid in water

**Example 11.5.2**

Write an equation for the reaction of decanoic acid with each compound.

a. aqueous sodium hydoxide (NaOH)
b. aqueous potassium hydroxide (KOH)

**Solution**

a. Decanoic acid has 10 carbon atoms. It reacts with NaOH to form a salt and water ($H_2O$). $CH_3(CH_2)_8COOH + NaOH(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell)$

b. With KOH, the products are a salt and $H_2O$. $CH_3(CH_2)_8COOH + KOH(aq) \rightarrow CH_3(CH_2)_8COO^-K^+(aq) + H_2O(\ell)$

**Exercise 11.5.3**

Write an equation for the reaction of benzoic acid with each compound.

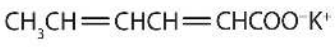
a. aqueous sodium hydroxide (NaOH)
b. aqueous potassium hydroxide (KOH)

## To Your Health: Organic Salts as Preservatives

Some organic salts are used as preservatives in food products. They prevent spoilage by inhibiting the growth of bacteria and fungi. Calcium and sodium propionate, for example, are added to processed cheese and bakery goods; sodium benzoate is added to cider, jellies, pickles, and syrups; and sodium sorbate and potassium sorbate are added to fruit juices, sauerkraut, soft drinks, and wine. Look for them on ingredient labels the next time you shop for groceries.



Calcium propionate



Potassium sorbate

## Concept Review Exercises

1. What products are formed when a carboxylic acid is neutralized with a strong base? What additional product is formed when a carboxylic acid is neutralized with a carbonate or a bicarbonate?

## Answers

1. A carboxylate salt and water.

## Key Takeaways

- Soluble carboxylic acids are weak acids in aqueous solutions.
- Carboxylic acids neutralize bases to form salts.

## Exercises

1. Write the equation for the ionization of $CH_3CH_2CH_2COOH$ in water.
2. Write the equation for the neutralization of $CH_3CH_2CH_2COOH$ with sodium hydroxide [NaOH(aq)].
3. Write the equation for the reaction of $CH_3COOH$ with potassium hydroxide [KOH(aq)].
4. Write the equation for the reaction of $CH_3CH_2COOH$ with sodium hydroxide [NaOH(aq)].
5. Write the equation for the ionization of propanoic acid in water.
6. Write the equation for the ionization of 4-chloropentanoic acid in water.
7. Write an equation for the reaction of benzoic acid with each compound.
   a. aqueous NaOH
   b. aqueous KOH

8. Write the condensed structural formula for each compound.

   a. potassium ethanoate
   b. lithium propanoate

9. Name each compound (IUPAC).

   a. $CH_3CH_2CH_2COO^-Li^+$
   b. $CH_3CH_2CH_2COO^-NH_4^+$

## Answers

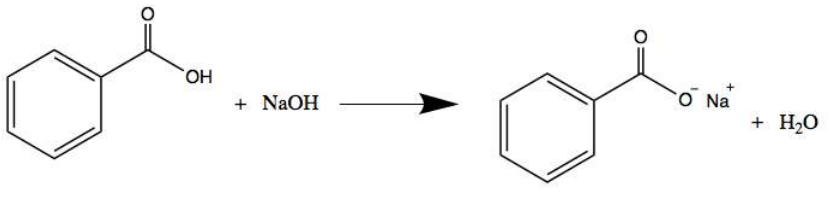
1. $CH_3CH_2CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2CH_2COO^-(aq) + H_3O^+(aq)$

3. $CH_3COOH + KOH(aq) \rightarrow 2CH_3COO^-K^+(aq) + H_2O(\ell)$

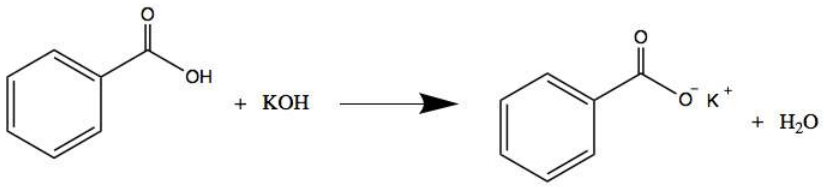
5. $CH_3CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$

7.

a.




b.



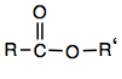

9. a. lithium butanoate  b. ammonium butanoate

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# 11.6: Esters - Structures and Names

**Learning Objectives**

- Identify the general structure for an ester.
- Use common names to name esters.
- Name esters according to the IUPAC system.

Esters have the general formula,  , where R may be a hydrogen atom, an alkyl group, or an aryl group, and R′ may be an alkyl group or an aryl group but *not* a hydrogen atom. (If it were hydrogen atom, the compound would be a carboxylic acid.) Figure **11.6.1** shows models for two common esters.

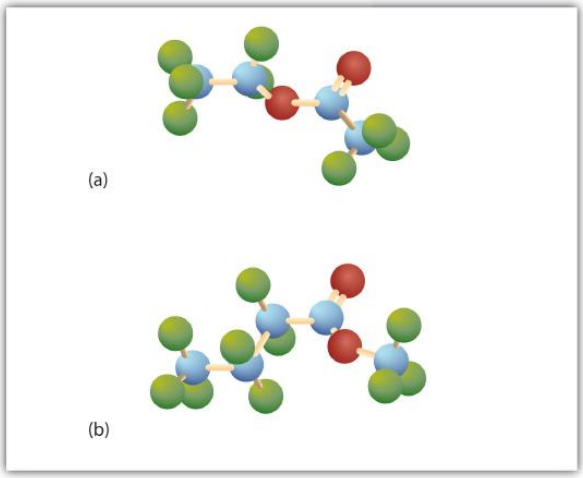



Figure **11.6.1**: The Structure of Esters. Esters feature a carbon-to-oxygen double bond that is also singly bonded to a second oxygen atom, which is then joined to an alkyl or an aryl group. The esters shown here are ethyl acetate (a) and methyl butyrate (b).

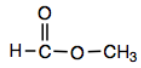
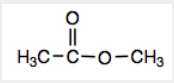
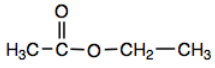
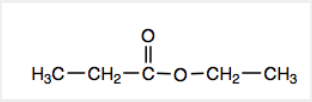
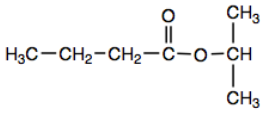
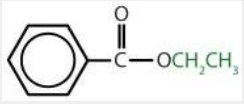
Esters occur widely in nature. Unlike carboxylic acids, esters generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers. Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.

Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

## Names of Esters

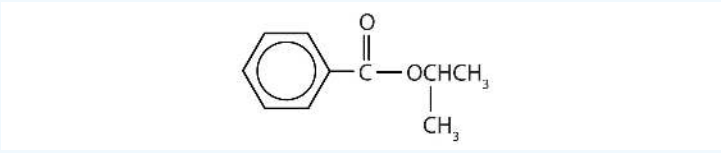
Although esters are covalent compounds and salts are ionic, esters are named in a manner similar to that used for naming salts. The group name of the alkyl or aryl portion is given first and is followed by the name of the acid portion. In both common and International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the *-ic* ending of the parent acid is replaced by the suffix *-ate* (Table **11.6.1**).

Table **11.6.1**: Nomenclature of Esters

| Condensed Structural Formula | Common Name | IUPAC Name |
|---|---|---|
|  | methyl formate | methyl methanoate |
|  | methyl acetate | methyl ethanoate |
|  | ethyl acetate | ethyl ethanoate |
|  | ethyl propionate | ethyl propanoate |
|  | isopropyl butyrate | isopropyl butanoate |
|  | ethyl benzoate | ethyl benzoate |

**Example 11.6.1**

Give the common and IUPAC names for each compound.

1. 
2. 

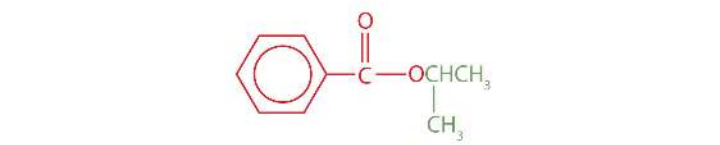
**Solution**

1. The alkyl group attached directly to the oxygen atom is a butyl group (in green).



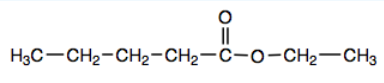
The part of the molecule derived from the carboxylic acid (in red) has three carbon atoms. It is called propionate (common) or propanoate (IUPAC). The ester is therefore butyl propionate or butyl propanoate.

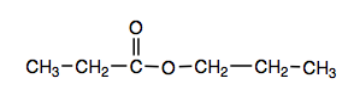
2. An alkyl group (in green) is attached directly to the oxygen atom by its middle carbon atom; it is an isopropyl group. The part derived from the acid (that is, the benzene ring and the carbonyl group, in red) is benzoate. The ester is therefore isopropyl benzoate (both the common name and the IUPAC name).



**Exercise 11.6.1**

Give the IUPAC names for each compound.

a. 

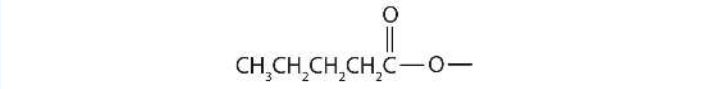
b. 

**Example 11.6.2**

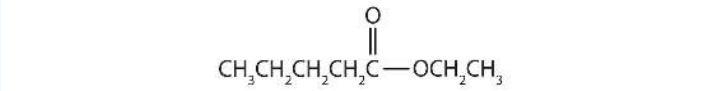
Draw the structure for ethyl pentanoate.

**Solution**

Start with the portion from the acid. Draw the pentanoate (five carbon atoms) group first; keeping in mind that the last carbon atom is a part of the carboxyl group.



Then attach the ethyl group to the bond that ordinarily holds the hydrogen atom in the carboxyl group.



**Exercise 11.6.2**

Draw the structure for phenyl pentanoate.

## Concept Review Exercises

1. From what carboxylic acid and what alcohol can isopropyl hexanoate be made?
2. From what carboxylic acid and what alcohol can cyclobutyl butanoate be made?

## Answers

1. hexanoic acid and 2-propanol
2. butanoic acid and cyclobutanol

## Key Takeaway

- An ester has an OR group attached to the carbon atom of a carbonyl group.

## Exercises

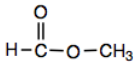
1. Draw the structure for each compound.
   a. methyl ethanoate
   b. ethyl pentanoate
   c. phenyl ethanoate

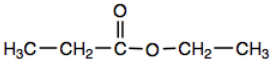
d. isopropyl propanoate

2. Draw the structure for each compound.

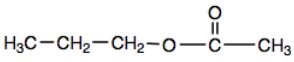
a. ethyl hexanoate
b. ethyl benzoate
c. phenyl benzoate
d. ethyl 3-methylhexanoate

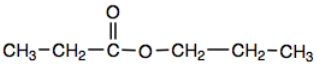
3. Name each compound with the IUPAC name.

a. 

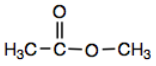
b. 

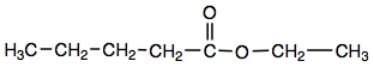
4. Name each compound with the IUPAC name.

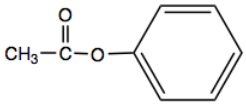
a. 

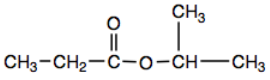
b. 

## Answers

1. a. 

b. 

c. 

d. 

3. a. methyl methanoate
b. ethyl propanoate

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# 11.7: Physical Properties of Esters

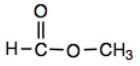
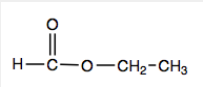
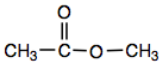
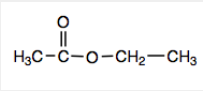
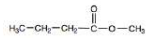
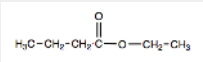
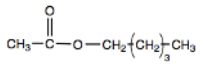
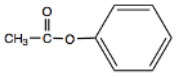
**Learning Objectives**

- Compare the boiling points of esters with alcohols of similar molar mass.
- Compare the solubilities of esters in water with the solubilities of comparable alkanes and alcohols in water.

Ester molecules are polar but have no hydrogen atom attached directly to an oxygen atom. They are therefore incapable of engaging in intermolecular hydrogen bonding with one another and thus have considerably lower boiling points than their isomeric carboxylic acids counterparts. Because ester molecules can engage in hydrogen bonding with water molecules, however, esters of low molar mass are somewhat soluble in water. Borderline solubility occurs in those molecules that have three to five carbon atoms. Table 11.7.1 lists the physical properties of some common esters.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer "dries," leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

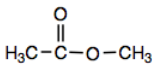
Table **11.7.1***: Physical Properties of Some Esters*

| Condensed Structural Formula | Name | Molar Mass | Melting Point (°C) | Boiling Point (°C) | Aroma |
|---|---|---|---|---|---|
|  | methyl methanoate | 60 | −99 | 32 | |
|  | ethyl methanoate | 74 | −80 | 54 | rum |
|  | methyl ethanoate | 74 | −98 | 57 | |
|  | ethyl ethanoate | 88 | −84 | 77 | |
|  | methyl butanoate | 102 | −85 | 102 | apple |
|  | ethyl butanoate | 116 | −101 | 121 | pineapple |
|  | pentyl ethanoate | 130 | −71 | 148 | pear |
| $CH_3COOCH_2CH_2CH(CH_3)_2$ | isopentyl ethanoate | 130 | −79 | 142 | banana |
|  | phenyl ethanoate | 150 | −51 | 215 | jasmine |
| $CH_3CH_2CH_2COO(CH_2)_4CH_3$ | pentyl butanoate | 158 | −73 | 185 | apricot |
| $CH_3COO(CH_2)_7CH_3$ | octyl ethanoate | 172 | −39 | 210 | orange |

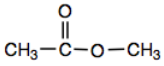
## Summary

Esters have polar bonds but do not engage in hydrogen bonding and are therefore intermediate in boiling points between the nonpolar alkanes and the alcohols, which engage in hydrogen bonding. Ester molecules can engage in hydrogen bonding with water, so esters of low molar mass are therefore somewhat soluble in water.

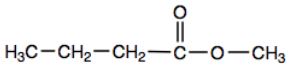
## Concept Review Exercises

1. Which compound has the higher boiling point— $CH_3$-$CH_2$-$CH_2$-$CH_2$-OH or  ? Explain.

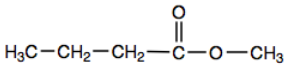
## Answers

1. $CH_3$-$CH_2$-$CH_2$-$CH_2$-OH because there is intermolecular hydrogen bonding (There is no intermolecular hydrogen bonding in  .)

## Exercises

1. Which compound has the higher boiling point— $CH_3$-$CH_2$-$CH_2$-COOH or  ? Explain.
2. Which compound is more soluble in water—methyl ethanoate or octyl ethanoate? Explain.

## Answer

1. $CH_3$-$CH_2$-$CH_2$-COOH because there is intermolecular hydrogen bonding and forms a dimer (There is no intermolecular hydrogen bonding between ethers  .)

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# 11.8: Preparation of Esters

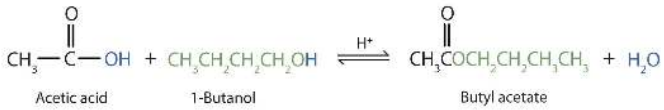
**Learning Objectives**

- To identify and describe the substances from which most esters are prepared.

Some esters can be prepared by esterification, a reaction in which a carboxylic acid and an alcohol, heated in the presence of a mineral acid catalyst, form an ester and water:



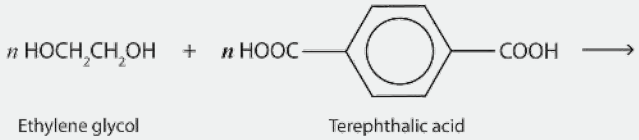

The reaction is reversible. As a specific example of an esterification reaction, butyl acetate can be made from acetic acid and 1-butanol.

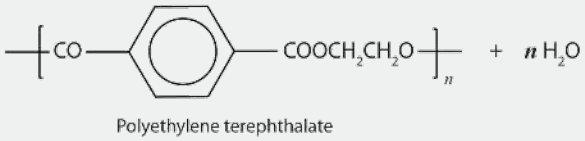



**A Closer Look: Condensation Polymers**

A commercially important esterification reaction is condensation polymerization, in which a reaction occurs between a dicarboxylic acid and a dihydric alcohol (diol), with the elimination of water. Such a reaction yields an ester that contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other end. Further condensation reactions then occur, producing polyester polymers.

The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:




Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes. Synthetic arteries can be made from PET, polytetrafluoroethylene, and other polymers.

## Summary

Esters are made by the reaction of a carboxylic acid with an alcohol, a process that is called esterification.

## Concept Review Exercises

1. From what carboxylic acid and what alcohol can the ester isopropyl nonanoate be made?
2. From what carboxylic acid and what alcohol can the ester cyclobutyl butanoate be made?

## Answers

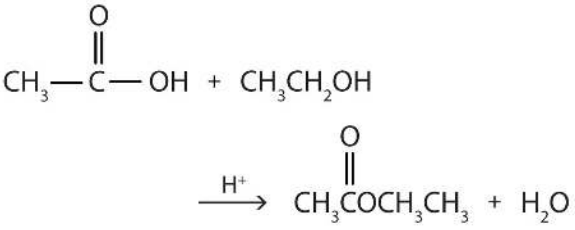
1. nonanoic acid and 2-propanol
2. butanoic acid and cyclobutanol

## Exercises

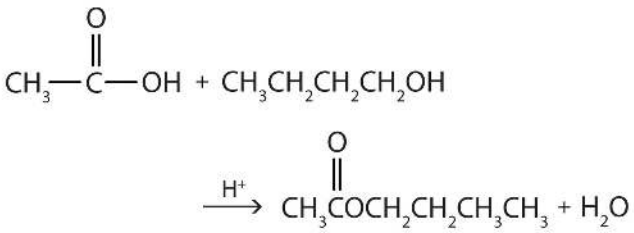
1. Write the equation for the reaction of ethanoic acid with each compound in the presence of a an acid catalyst.
   a. ethanol
   b. 1-butanol
2. Write the equation for the reaction of benzoic acid with each compound in the presence of a an acid catalyst.
   a. methanol
   b. 1-propanol

## Answer

1. a.



b.



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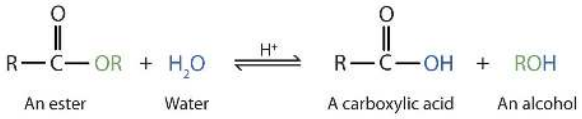
# 11.9: Hydrolysis of Esters

**Learning Objectives**

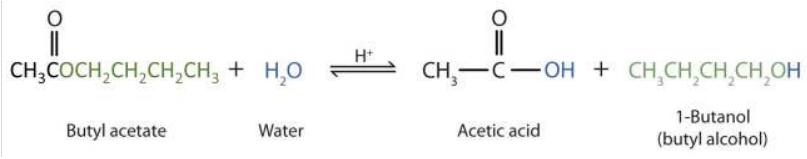
- Describe the typical reaction that takes place with esters.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.

Esters are neutral compounds, unlike the acids from which they are formed. In typical reactions, the alkoxy (OR′) group of an ester is replaced by another group. One such reaction is hydrolysis, literally "splitting with water." The hydrolysis of esters is catalyzed by either an acid or a base.

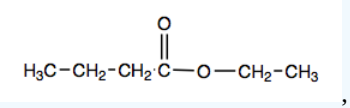
Acidic hydrolysis is simply the reverse of esterification. The ester is heated with a large excess of water containing a strong-acid catalyst. Like esterification, the reaction is reversible and does not go to completion.




As a specific example, butyl butanoate and water react to form ethanoic acid and 1-butanol. The reaction is reversible and does not go to completion.

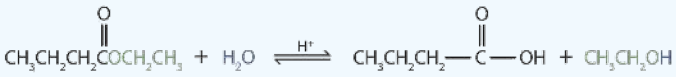



**Example 11.9.1**

Write an equation for the acidic hydrolysis of ethyl butanoate,  , and name the products.

**Solution**

Remember that in acidic hydrolysis, water (HOH) splits the ester bond. The H of HOH joins to the oxygen atom in the OR part of the original ester, and the OH of HOH joins to the carbonyl carbon atom:

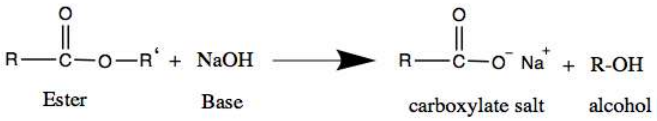



The products are butanoic acid and ethanol.

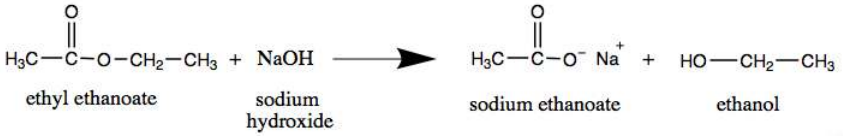
**Exercise 11.9.1**

Write an equation for the acidic hydrolysis of methyl butanoate and name the products.

When a base (such as sodium hydroxide [NaOH] or potassium hydroxide [KOH]) is used to hydrolyze an ester, the products are a carboxylate salt and an alcohol. Because soaps are prepared by the alkaline hydrolysis of fats and oils, alkaline hydrolysis of esters is called saponification (Latin *sapon*, meaning "soap," and *facere*, meaning "to make"). In a saponification reaction, the base is a reactant, not simply a catalyst. The reaction goes to completion:




As a specific example, ethyl acetate and NaOH react to form sodium acetate and ethanol:

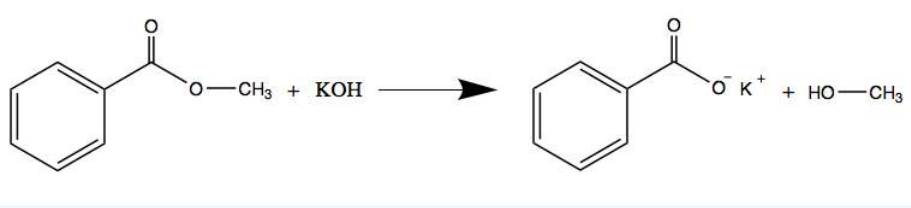



**Example 11.9.2**

Write an equation for the hydrolysis of methyl benzoate in a potassium hydroxide solution.

**Solution**

In basic hydrolysis, the molecule of the base splits the ester linkage. The acid portion of the ester ends up as the *salt* of the acid (in this case, the potassium salt). The alcohol portion of the ester ends up as the free alcohol.



**Exercise 11.9.2**

Write the equation for the hydrolysis of ethyl propanoate in a sodium hydroxide solution.

## Summary

Hydrolysis is a most important reaction of esters. Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol. Basic hydrolysis of an ester gives a carboxylate salt and an alcohol.

## Concept Review Exercises

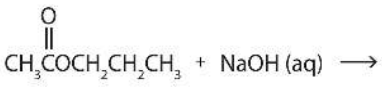
1. How do acidic hydrolysis and basic hydrolysis of an ester differ in terms of the products obtained?
2. What is saponification?

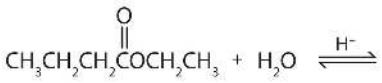
## Answers

1. acidic hydrolysis: carboxylic acid + alcohol; basic hydrolysis: carboxylate salt + alcohol
2. the basic hydrolysis of an ester

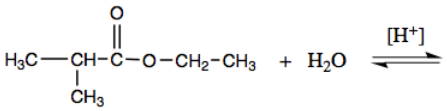
## Exercises

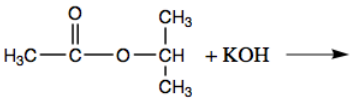
1. Write an equation for the acid-catalyzed hydrolysis of ethyl ethanoate.
2. Write an equation for the base-catalyzed hydrolysis of ethyl ethanoate.
3. Complete each equation.

a. 

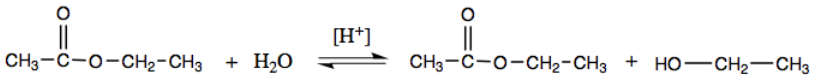
b. 

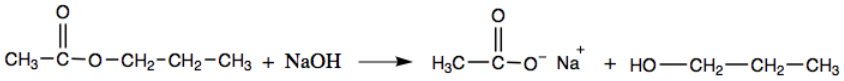
4. Complete each equation.

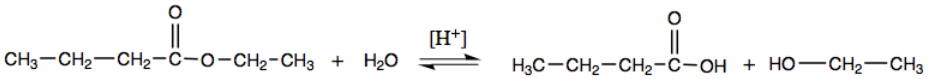
a. 

b. 

## Answers

1. 

3. a. 

b. 

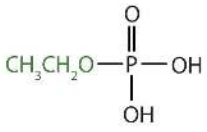
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# 11.10: Esters of Phosphoric Acid

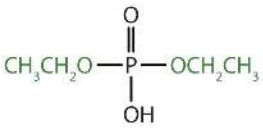
**Learning Objectives**

- Describe phosphate esters.
- Understand why phosphate esters are important in living cells.

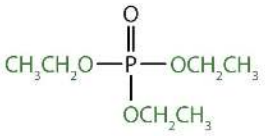
Just as carboxylic acids do, inorganic acids such as nitric acid ($HNO_3$), sulfuric acid ($H_2SO_4$), and phosphoric acid ($H_3PO_4$) also form esters. The esters of phosphoric acid are especially important in biochemistry. A phosphoric acid molecule can form a monoalkyl, a dialkyl, or a trialkyl ester by reaction with one, two, or three molecules of an alcohol.



Ethyl dihydrogen phosphate

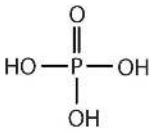


Diethyl hydrogen phosphate

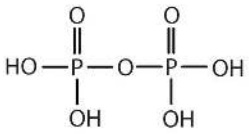


Triethyl phosphate

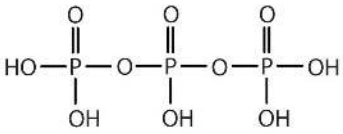
Esters of pyrophosphoric acid and triphosphoric acid are also important in biochemistry.



Phosphoric acid



Pyrophosphoric acid

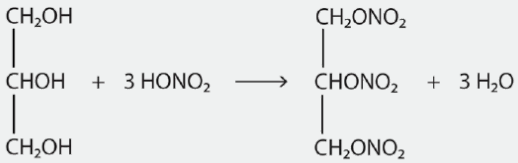


Triphosphoric acid

Esters of these acids are present in every plant and animal cell. They are biochemical intermediates in the transformation of food into usable energy. The bonds between phosphate units in adenosine triphosphate (ATP) are called **phosphoanhydride bonds**. These are high-energy bonds that store energy from the metabolism of foods. Hydrolysis of ATP releases energy as it is needed for biochemical processes (for instance, for muscle contraction). Phosphate esters are also important structural constituents of phospholipids and nucleic acids.

**Nitroglycerin**

The explosive nitroglycerin (glyceryl trinitrate) is an ester formed from glycerol and nitric acid. It is used in medicine to relieve chest pain in heart disease.



Glycerol

Glycerol trinitrate (nitroglycerin)

**11.10.1 Exercise**

What compounds combine to form phosphate esters?

**Answer**

phosphoric acids and alcohols

## Summary

Inorganic acids such as $H_3PO_4$ form esters. The esters of phosphoric acid are especially important in biochemistry.

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# 12: Organic Bases and Some of Their Derivatives Part 2

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# 12.1: Amines - Structures and Names

**Learning Objectives**

- Identify the general structure for an amine.
- Identify the functional group for amines.
- Determine the structural feature that classifies amines as primary, secondary, or tertiary.
- Use nomenclature systems to name amines.

Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A primary (1°) amine has one alkyl (or aryl) group on the nitrogen atom, a secondary (2°) amine has two, and a tertiary (3°) amine has three (Figure **12.1.1**).

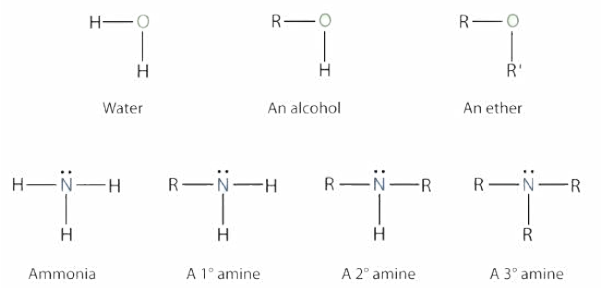
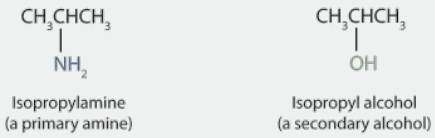



Figure **12.1.1**: The Structure of Amines Compared to Water, an Alcohol, and an Ether

To classify alcohols, we look at the number of carbon atoms bonded to the *carbon atom* bearing the OH group, not the oxygen atom itself. Thus, although isopropylamine looks similar to isopropyl alcohol, the former is a *primary* amine, while the latter is a *secondary* alcohol.

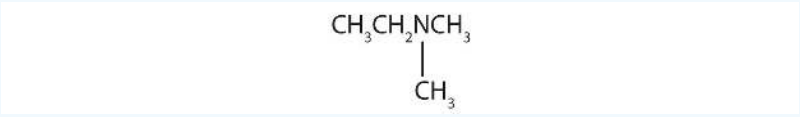


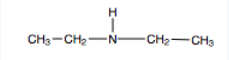

The common names for simple aliphatic amines consist of an alphabetic list of alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*. (Systematic names are often used by some chemists.) The amino group ($NH_2$) is named as a substituent in more complicated amines, such as those that incorporate other functional groups or in which the alkyl groups cannot be simply named.

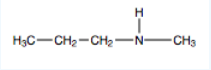
**Example 12.1.1**

Give the IUPAC name and classify each compound.

a. $CH_3CH_2CH_2NH_2$

b. 

c. 

d. 

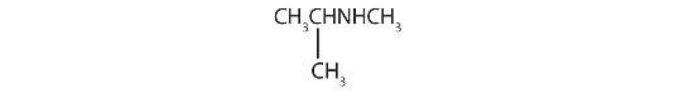
**Solution**

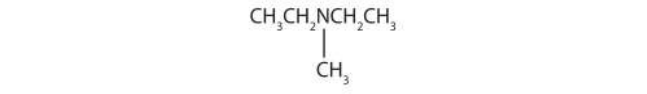
a. There is only one carbon grooup attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (propane) is attached to the $NH_2$ group through an end carbon atom, so the name is 1-propanamine.

b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is a tertiary amine. The IUPAC name would be N,N-dimethylethanamine
c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, its IUPAC name is N-ethylethanamine.
d. The nitrogen atom has a methyl group and a propyl group, so the IUPAC name is N-methyl-1-propanamine, a secondary amine.

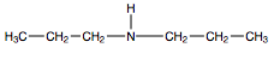
## Exercise 12.1.1

Provide the IUPAC name and classify each compound.

a. 


b. 


c. $CH_3CH_2CH_2CH_2NH_2$

d. 

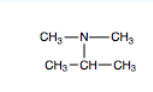

## Example 12.1.2

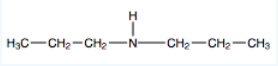
Draw the structure for each compound and classify.

a. N,N-dimethyl-2-propanamine
b. N-propyl-1-propanamine

**Solution**

a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.



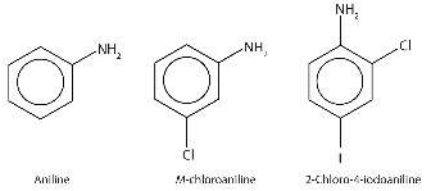

b. The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) 


## Exercise 12.1.2

Draw the structure for each compound and classify.

a. N-ethyl-2-propanamine
b. N,N-diethy-1-propanamine

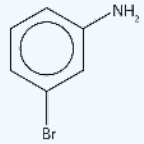
The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—aniline. Aryl amines are named as derivatives of aniline.




Aniline M-chloroaniline 2-Chloro-4-iodoaniline

**Example 12.1.3**

Name this compound.

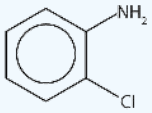



**Solution**

The benzene ring with an amino ($NH_2$) group is aniline. The compound is named as a derivative of aniline: 3-bromoaniline or *m*-bromoaniline.

**Exercise 12.1.3**

Name this compound using both the IUPAC and common.

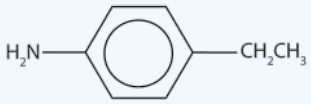



**Example 12.1.4**

Draw the structure for *p*-ethylaniline and classify.

**Solution**

The compound is a derivative of aniline. It is a primary amine having an ethyl group located *para* to the amino ($NH_2$) group.




**Exercise 12.1.4**

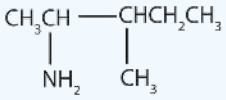
Draw the structure for *p*-isopropylaniline and classify.

**Example 12.1.5**

Draw the structure for 3-methyl-2-pentanamine.

**Solution**

Always start with the parent compound: draw the pentane chain. Then attach a methyl group at the third carbon atom and an amino group at the second carbon atom.




**Exercise 12.1.5**

Draw the structure for 3-ethyl-1-chloro-2-heptanamine.

Ammonium ($NH_4^+$) ions, in which one or more hydrogen atoms are replaced with alkyl groups, are named in a manner analogous to that used for simple amines. The alkyl groups are named as substituents, and the parent species is regarded as the $NH_4^+$ ion. For example, $CH_3NH_3^+$ is the methylammonium ion. The ion formed from aniline ($C_6H_5NH_3^+$) is called the anilinium ion.

**Example 12.1.6**

Name each ion.

a. $CH_3NH_3^+$
b. $(CH_3)_2NH_2^+$
c. $(CH_3)_3NH^+$
d. $(CH_3)_4N^+$

**Solution**

The ions have one, two, three, and four methyl ($CH_3$) groups attached to a nitrogen atom. Their names are as follows:

a. methylammonium ion
b. dimethylammonium ion
c. trimethylammonium ion
d. tetramethylammonium ion

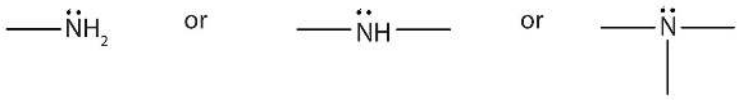
**Exercise 12.1.6**

Name each ion.

a. $CH_3CH_2NH_3^+$
b. $(CH_3CH_2)_3NH^+$
c. $(CH_3CH_2CH_2)_2NH_2^+$
d. $(CH_3CH_2CH_2CH_2)_4N^+$

## Summary

An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. The amine functional group is as follows:




Amines are classified as primary, secondary, or tertiary by the number of hydrocarbon groups attached to the nitrogen atom. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

## Concept Review Exercises

1. To what inorganic compound are the amines related?
2. How are amines classified?

## Answers

1. ammonia
2. by the number of hydrocarbon groups on the nitrogen atom: primary amine, one group; secondary amine, two groups; tertiary amine, three groups

## Exercises

1. Draw the structure for each compound and classify the amine as primary, secondary, or tertiary.
   a. N-methylmethanamine
   b. N-ethyl-N-methylethanamine
   c. 2-aminoethanol
2. Draw the structure for each compound and classify the amine as primary, secondary, or tertiary.

a. 3-pentanamine
b. 1,6-hexanediamine
c. N-ethylaniline

3. Draw the structure for each compound.

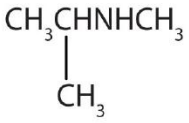
a. aniline
b. *m*-bromoaniline

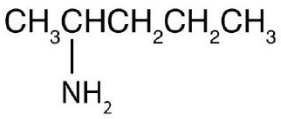
4. Draw the structure for each compound.

a. 2-chloroaniline
b. 3,5-dichloroaniline

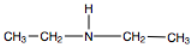
5. Name each compound using IUPAC form.

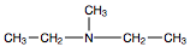
a. $CH_3CH_2CH_2NH_2$

b. 

c. 

6. Name each compound.

a. 

b. 

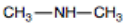
7. Draw the structure for each compound.

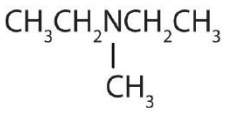
a. dimethylammonium chloride
b. anilinium chloride

8. Draw the structure for each compound.

a. ethylmethylammonium chloride

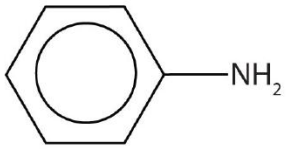
## Answers

1. a.  ; secondary
   b. tertiary

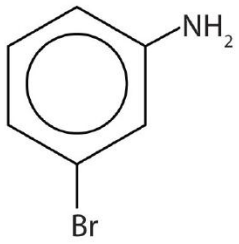


c.  ; primary

3. a.

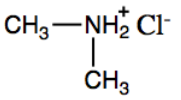



b.

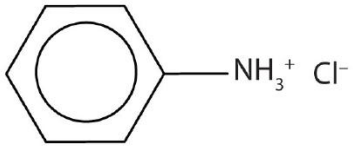



5. a. 1-propanamine
   b. N-ethyl-2-propanamine
   c. 2-pentanamine

7. a.




b.




---

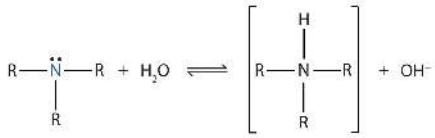
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# 12.2: Amines as Bases

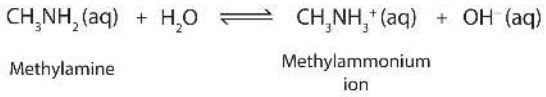
**Learning Objectives**

- Name the typical reactions that take place with amines.
- Describe heterocyclic amines.

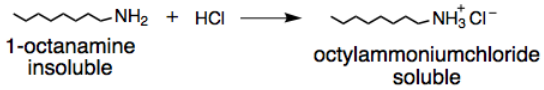
Recall that ammonia ($NH_3$) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. Amines also have a lone electron pair on their nitrogen atoms and can accept a proton from water to form substituted ammonium ($NH_4^+$) ions and hydroxide ($OH^-$) ions:



As a specific example, methylamine reacts with water to form the methylammonium ion and the $OH^-$ ion.

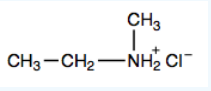



Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.

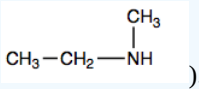



Amine salts are named like other salts: the name of the cation is followed by the name of the anion.

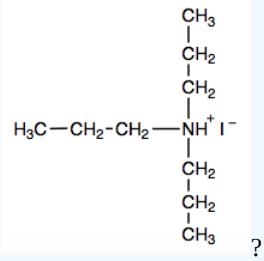
**Example 12.2.1**

What are the formulas of the acid and base that react to form  ?

**Solution**

The cation has two groups—methyl and ethyl—attached to the nitrogen atom. It comes from N-methylethanamine (  ). The anion is the chloride ion. It comes from hydrochoric acid (HCl).

**Exercise 12.2.1**

What are the formulas of the acid and base that react to form  ?

### To Your Health: Amine Salts as Drugs

Salts of aniline are properly named as *anilinium* compounds, but an older system, still in use for naming drugs, identifies the salt of aniline and hydrochloric acid as "aniline hydrochloride." These compounds are ionic—they are salts—and the properties of the compounds (solubility, for example) are those characteristic of salts. Many drugs that are amines are converted to hydrochloride salts to increase their solubility in aqueous solution.

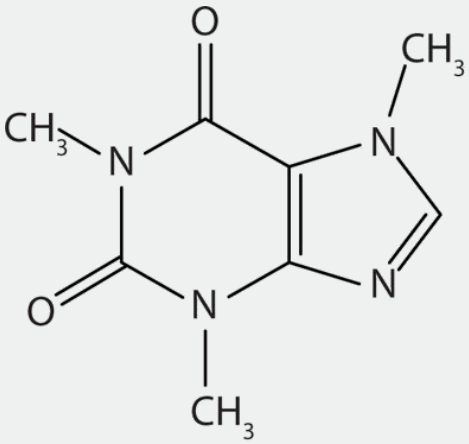
## Heterocyclic Amines

Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning "other"), nitrogen, oxygen, sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means "like alkalis." Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

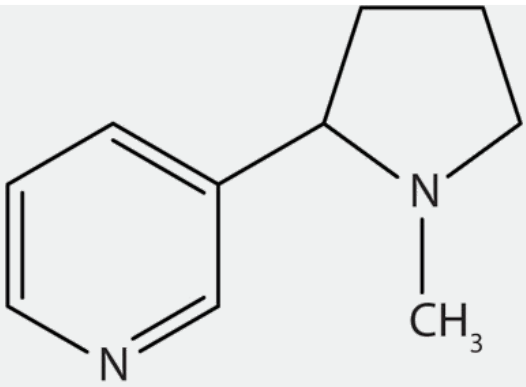
### To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



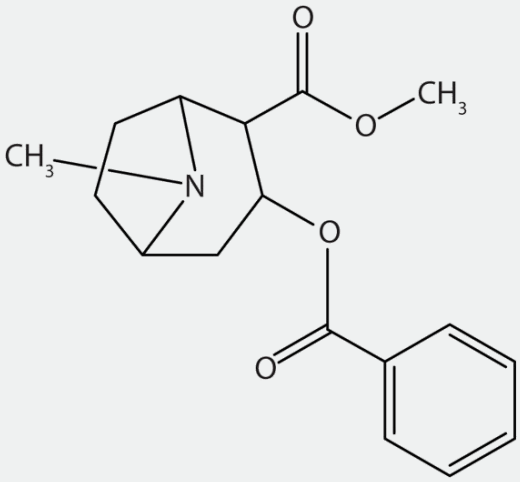

Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



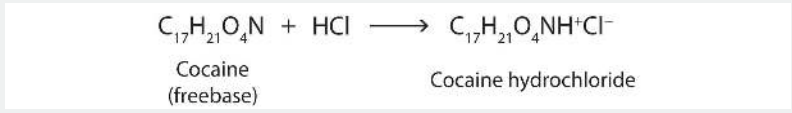

Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.




Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.




Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

## Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called "hydrochlorides." Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

## Concept Review Exercises

1. Explain the basicity of amines.
2. Contrast the physical properties of amines with those of alcohols and alkanes.
3. What is a heterocyclic compound?

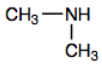
## Answers

1. Amines have a lone pair of electrons on the nitrogen atom and can thus act as proton acceptors (bases).
2. The solubilities of amines are similar to those of alcohols; the boiling points of primary and secondary amines are similar to those of alcohols; the boiling points of tertiary amines, which cannot engage in hydrogen bonding because they do not have a hydrogen atom on the nitrogen atom, are comparable to those of alkanes.
3. Heterocyclic compounds are ring compounds with atoms other than carbon atoms in the ring.

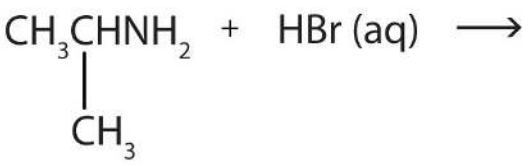
## Exercises

1. What salt is formed in each reaction? Write its condensed structural formula.

   a. $CH_3NH_2(aq) + HBr(aq) \rightarrow$

   b.  (aq) + HCl(aq) →

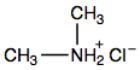
2. What salt is formed in each reaction? Draw its structure.

   a. 

   b. 

## Answer

1. a. $CH_3NH_3^+Br^-(aq)$

   b.  (aq)

---

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# 12.3: Physical Properties of Amines

**Learning Objectives**

- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Primary and secondary amines have hydrogen atoms bonded to an nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure **12.3.1**), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine ($CH_3NH_2$; −6°C) with those of ethane ($CH_3CH_3$; −89°C) and methanol ($CH_3OH$; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table **12.3.1**).

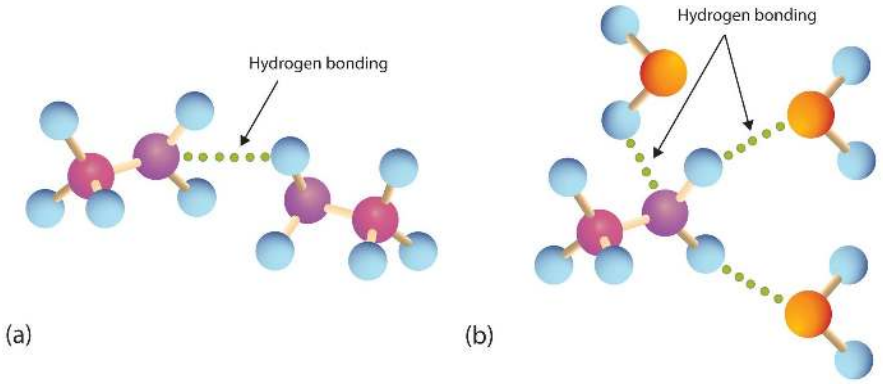
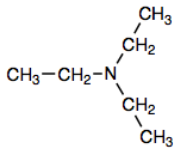



Figure **12.3.1**: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

Table **12.3.1**: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds

| Name | Condensed Structural Formula | Class | Solubility in 25 mL Water |
|---|---|---|---|
| 1-butamine | $CH_3$-$CH_2$-$CH_2$-$CH_2$-$NH_2$ | 1° | miscible |
| N-ethylethan | $CH_3$-$CH_2$-NH-$CH_2CH_3$ | 2° | [illegible] miscible |

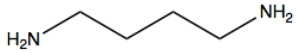
| | | | |
|---|---|---|---|
| amine | | | |
| 1-butanol | $CH_3$-$CH_2$-$CH_2$-$CH_2OH$ | — | 117.148 |
| N-propyl-1-propanamine | $CH_3$-$CH_2$-$CH_2$-NH-$CH_2$-$CH_2$-$CH_3$ | 2° | 101.191 |
| N,N-diethylethana |  | 3° | 101.191 |

| | | |
|---|---|---|
| n a m i n e | | |
| p r o p o x y - 1 - p r o p a n e | $CH_3$-$CH_2$-$CH_2$-O-$CH_2$-$CH_2$-$CH_3$ | — |

All three classes of amines can engage in hydrogen bonding with water (Figure 12.3.1*b*). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

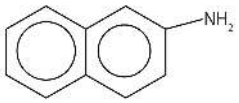
### To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.



Putrescine

Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.




## Key Takeaways

- Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in intermolecular hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative.
- The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass.
- Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

## Concept Review Exercises

1. Which compound has the higher boiling point, $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$NH_2$ or $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$? Explain.
2. Which compound is more soluble in water, $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_3$ or $CH_3$-$CH_2$-NH-$CH_2$-$CH_3$? Explain.

## Answers

1. $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$NH_2$ because the nitrogen-to-hydrogen (N–H) bonds can engage in hydrogen bonding;

   $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_3$ cannot engage in hydrogen bonding
2. $CH_3$-$CH_2$-NH-$CH_2$-$CH_3$ because amines can engage in hydrogen bonding with water;

   alkanes cannot engage in hydrogen bonding

## Exercises

1. Which compound of each pair has the higher boiling point? Explain.

   a. 1-butanamine or pentane
   b. $CH_3$-$NH_2$ or $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$NH_2$
2. Which compound of each pair has the higher boiling point? Explain.

   a. 1-butanamine or 1-butanol
   b. trimethylamine (N,N-dimethylmethanamine) or 1-propanamine
3. Which compound is more soluble in water—$CH_3$-$CH_2$-$CH_3$ or $CH_3$-$CH_2$-$NH_2$? Explain.
4. Which compound is more soluble in water—$CH_3$-$CH_2$-$CH_2$-$NH_2$ or $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$NH_2$? Explain.

## Answers

1. a. 1-butanamine because the N–H bonds can engage in hydrogen bonding; pentane cannot engage in hydrogen bonding
   b. $CH_3$-$CH_2$-$CH_2$-$CH_2$-$CH_2$-$NH_2$ because it has a longer carbon chain and therefore exhibit greater LDF than $CH_3NH_2$
3. $CH_3$-$CH_2$-$NH_2$? because amines can engage in hydrogen bonding with water; alkanes cannot engage in hydrogen bonding

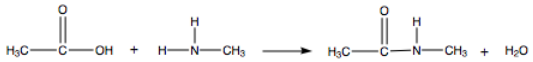
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# 12.4: Formation of Amides

**Learning Objectives**

- To describe the preparation procedure for amides.

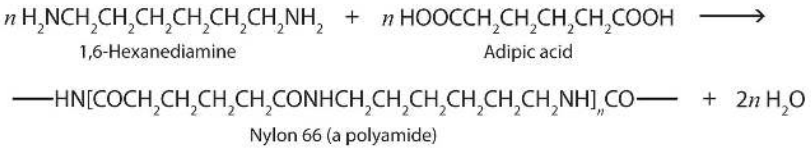
The addition of ammonia ($NH_3$) to a carboxylic acid forms an amide, but the reaction is very slow in the laboratory at room temperature. Water molecules are split out, and a bond is formed between the nitrogen atom and the carbonyl carbon atom.



In living cells, amide formation is catalyzed by enzymes. Proteins are polyamides; they are formed by joining amino acids into long chains. In proteins, the amide functional group is called a *peptide bond*.

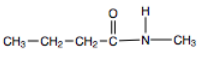
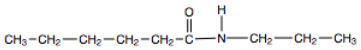
## Polyamides

Just as the reaction of a diol and a diacid forms a polyester, the reaction of a diacid and a diamine yields a polyamide. The two difunctional monomers often employed are adipic acid and 1,6-hexanediamine. The monomers condense by splitting out water to form a new product, which is still difunctional and thus can react further to yield a polyamide polymer.




Some polyamides are known as *nylons*. Nylons are among the most widely used synthetic fibers—for example, they are used in ropes, sails, carpets, clothing, tires, brushes, and parachutes. They also can be molded into blocks for use in electrical equipment, gears, bearings, and valves.

## Concept Review Exercises

1. Write the condensed structural formulas and give names of the two compounds from which N-methylbutanamide,  , is formed.
2. Write the condensed structural formulas and names of the two compounds from which  is formed.

## Answers

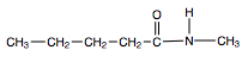
1. $CH_3CH_2CH_2COOH$ (butanoic acid) and $CH_3$-$NH_2$ (methanamine)
2. $CH_3CH_2CH_2CH_2CH_2COOH$ (hexanoic acid) and $CH_3CH_2CH_2NH_2$ (1-propanamine)

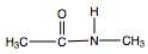
## Key Takeaway

- Amides are prepared by the reaction of a carboxylic acid with ammonia or an amine.

## Exercises

1. Write the condensed structural formulas and names of the two compounds from which N-methylpentanamide

(  ) is formed.

2. Write the condensed structural formulas and names of the two compounds from which  is formed.

## Answer

1. $CH_3CH_2CH_2CH_2COOH$ (pentanoic acid) and $CH_3$-$NH_2$ (methanamine)

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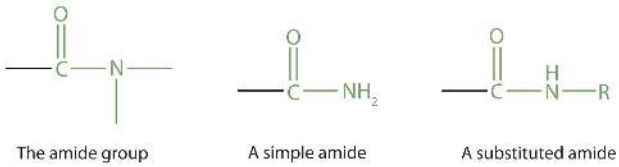
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# 12.5: Amides- Structures and Names

**Learning Objectives**

- Identify the general structure for an amide.
- Identify the functional group for an amide.
- Names amides with common names.
- Name amides according to the IUPAC system.

The amide functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*.



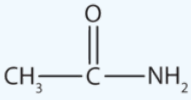

The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

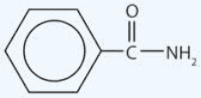
Simple amides are named as derivatives of carboxylic acids. The *-ic* ending of the common name or the *-oic* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.




**Example 12.5.1**

Name each compound with the common name, the IUPAC name, or both.

a. 

b. 

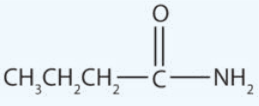
**Solution**

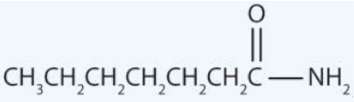
a. This amide has two carbon atoms and is thus derived from acetic acid. The OH of acetic acid is replaced by an $NH_2$ group. The *-ic* from *acetic* (or *-oic* from ethanoic) is dropped, and *-amide* is added to give *acetamide* (or ethanamide in the IUPAC system).

b. This amide is derived from benzoic acid. The *-oic* is dropped, and *-amide* is added to give benzamide.

**Exercise 12.5.1**

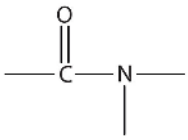
Name each compound with the IUPAC name.

a. 

b. 

## Key Takeaways

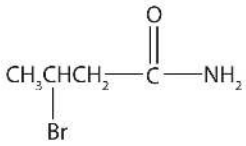
- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.
- The functional group for an amide is as follows:



- In names for amides, the *-ic acid* of the common name or the *-oic* ending of the IUPAC for the corresponding carboxylic acid is replaced by *-amide*.

## Concept Review Exercises

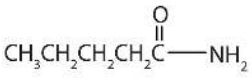
1. Name this compound with the common name and the IUPAC name.



2. Draw a the structural formulae for pentanamide.

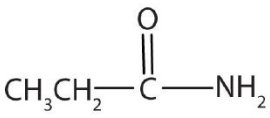
## Answers

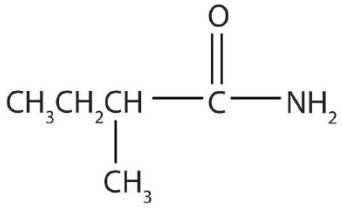
1. β-bromobutyramide (IUPAC: 3-bromobutanamide)

2. 

## Exercises

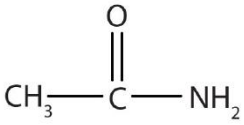
1. Draw the structure for each compound.
    a. methanamide
    b. hexanamide
2. Draw the structure for each compound.
    a. propanamide or propionamide (common name)
    b. butanamide
3. Name each compound with the IUPAC name.

a. 



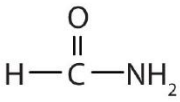
b.

4. Name the compound.



## Answers

1. a.



b.



3. a. IUPAC: propanamide
   b. IUPAC: 2-methylbutanamide

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# 12.6: Physical Properties of Amides

**Learning Objectives**

- Compare the boiling points of amides with alcohols of similar molar mass.
- Compare the solubilities in water of amides of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

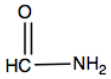
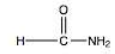
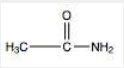
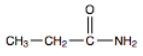
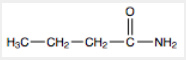
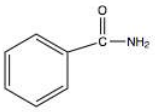
With the exception of methanamide (common name: formamide) (  ), which is a liquid, all simple amides are solids (Table **12.6.1**). The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms. Like the esters, solutions of amides in water usually are neutral—neither acidic nor basic.

Table **12.6.1**: *Physical Constants of Some Unsubstituted Amides*

| Condensed Structural Formula | Name common or IUPAC | Melting Point (°C) | Boiling Point (°C) | Solubility in Water |
|---|---|---|---|---|
|  | formamide or methanamide | 2 | 193 | soluble |
|  | acetamide or ethanamide | 82 | 222 | soluble |
|  | propionamide or propanamide | 81 | 213 | soluble |
|  | butyramide or butanamide | 115 | 216 | soluble |
|  | benzamide | 132 | 290 | slightly soluble |

The amides generally have high boiling points and melting points. These characteristics and their solubility in water result from the polar nature of the amide group and hydrogen bonding (Figure **12.6.1**). (Similar hydrogen bonding plays a critical role in determining the structure and properties of proteins, deoxyribonucleic acid [DNA], ribonucleic acid [RNA], and other giant molecules so important to life processes.

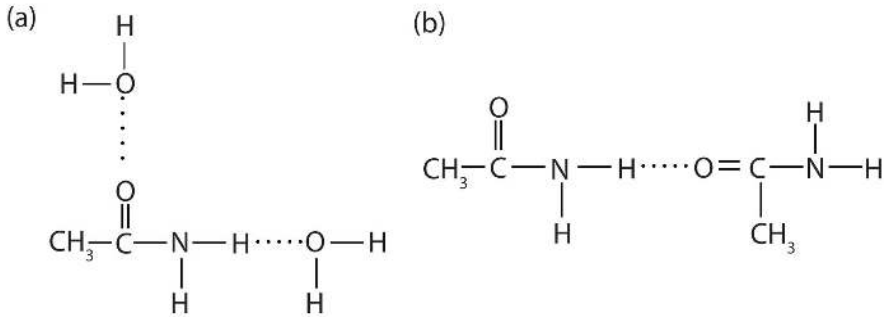
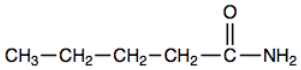
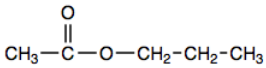
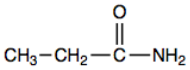



Figure **12.6.1**: Hydrogen Bonding in Amides. Amide molecules can engage in hydrogen bonding with water molecules (a). Those amides with a hydrogen atom on the nitrogen atom can also engage in hydrogen bonding (b). Both hydrogen bonding networks extend in all directions.

## Concept Review Exercises

1. Which compound has the higher boiling point—pentanamide,  , or propyl ethanoate,  , ? Explain.
2. Which compound is more soluble in water—propanamide  or 1-pentene, $CH_2$=CH-$CH_2$-$CH_2$-$CH_3$, ? Explain.

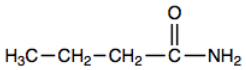
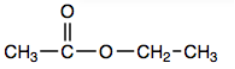
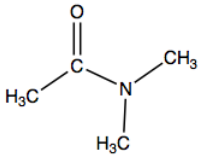
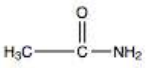
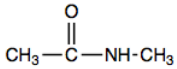
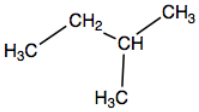
## Answers

1. pentanamide because the nitrogen-to-hydrogen (N–H) and the carbon-to-oxygen double (C=O) bonds can engage in hydrogen bonding; propyl acetate cannot engage in hydrogen bonding
2. propanamide because the N–H and C=O bonds can engage in hydrogen bonding with water; 1-pentene cannot engage in hydrogen bonding with water

## Key Takeaways

- Most amides are solids at room temperature; the boiling points of amides are much higher than those of alcohols of similar molar mass.
- Amides of six or fewer carbon atoms are soluble in water.

## Exercises

1. Which compound has the higher boiling point—butanamide,  , or ethyl ethanoate,  , ? Explain.
2. Which compound has the higher boiling point—butanamide or N,N-dimethylethanamide  ? Explain.
3. Which compound is more soluble in water—ethanamide,  , or 1-butene, $CH_2$=CH-$CH_2$-$CH_3$, ? Explain.
4. Which compound is more soluble in water— N-methylethanamide,  , or 2-methylbutane,  , ? Explain.

## Answers

1. Butanamide because the nitrogen-to-hydrogen (N–H) and the carbon-to-oxygen double (C=O) bonds can engage in hydrogen bonding; ethyl ethanoate cannot engage in hydrogen bonding

3. Ethanamide because the N–H and C=O bonds can engage in hydrogen bonding with water; 1-butene cannot engage in hydrogen bonding with water

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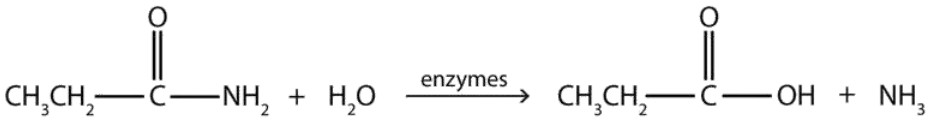
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# 12.7: Chemical Properties of Amides- Hydrolysis

**Learning Objectives**

- To identify the typical reaction that amides undergo.

Generally, amides resist hydrolysis in plain water, even after prolonged heating. In the presence of added acid or base, however, hydrolysis proceeds at a moderate rate. In living cells, amide hydrolysis is catalyzed by enzymes. Amide hydrolysis is illustrated in the following example:




> *Hydrolysis of an amide in acid solution actually gives a carboxylic acid and the salt of ammonia or an amine (the ammonia or amine initially formed is neutralized by the acid). Basic hydrolysis gives a salt of the carboxylic acid and ammonia or an amine.*

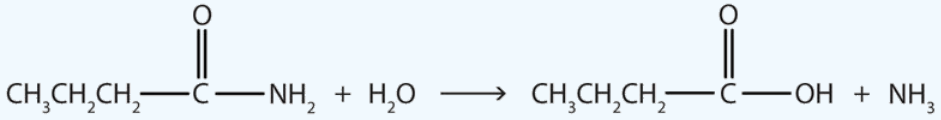
**Example 12.7.1**

Write the equation for the hydrolysis of each compound.

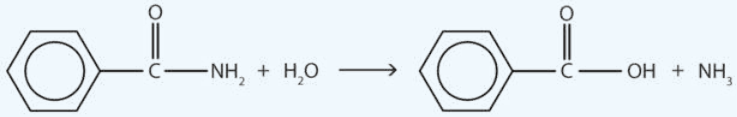
a. butanamide
b. benzamide

**Solution**

a. The hydrolysis of a simple amide produces an organic acid and ammonia. Butanamide thus yields butanoic acid and ammonia.




b. The hydrolysis of an amide produces an organic acid and ammonia. Benzamide thus yields benzoic acid and ammonia.




**Exercise 12.7.1**

Write the equation for the hydrolysis of each compound.

a. propanamide
b. hexanamide

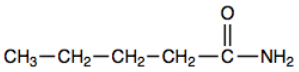
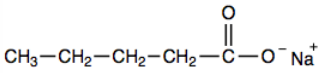
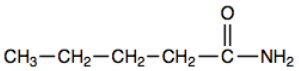
**Career Focus: Athletic Trainer**

Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology, chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding

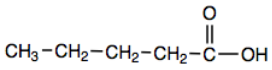
pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.

Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

## Concept Review Exercises

1. What are the products of the acid hydrolysis of an amide?
2. When the amide  is hydrolyzed in an NaOH solution, the products are  and $NH_3$. What products are obtained when  is hydrolyzed in an hydrochloric acid solution?

## Answers

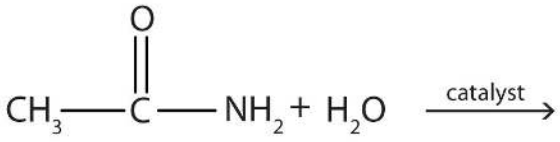
1. a carboxylic acid and ammonia or an amine
2. a  and $NH_4Cl$

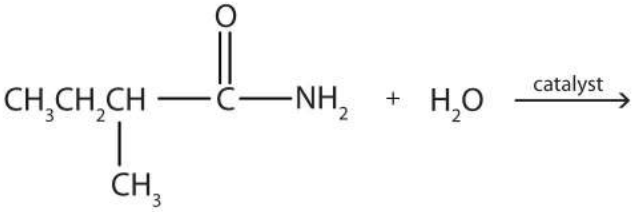
## Key Takeaway

- The hydrolysis of an amide produces a carboxylic acid and ammonia or an amine.

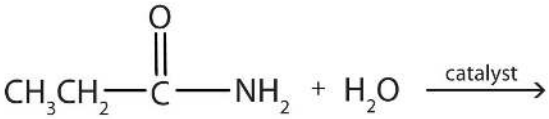
## Exercises

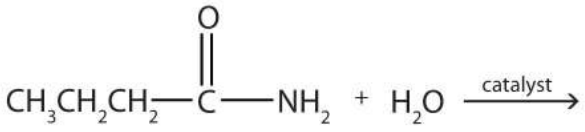
1. Complete the acid hydrolysis for the following reactions.

a. 

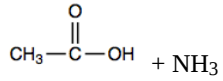
b. 

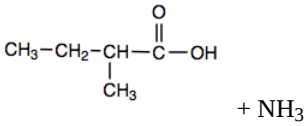
2. Complete acid hydrolyisis of the following reactions.

a. 

b. 


## Answer

1. a. 


b. 


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# 12.S: Organic Acids and Bases and Some of Their Derivatives (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the summary and ask yourself how they relate to the topics in the chapter.*

A **carboxylic acid** (RCOOH) contains the functional group COOH, called the **carboxyl group**, which has an OH group attached to a carbonyl carbon atom. An **ester** (RCOOR′) has an OR′ group attached to a carbonyl carbon atom. An **amine** is derived from ammonia ($NH_3$), with one, two, or all three of the hydrogen atoms of $NH_3$ replaced by an alkyl (or an aryl) group. The **amide** functional group has a carbonyl group joined to a nitrogen atom from $NH_3$ or an amine.

There are many familiar carboxylic acids. The R group may be a hydrogen atom (as in formic acid, HCOOH), an alkyl group (as in acetic acid, $CH_2COOH$), or an aryl group (as in benzoic acid, $C_6H_5COOH$). The location of substituents along the carbon chain is indicated by a Greek letter (for common names) or a number (for names from the International Union of Pure and Applied Chemistry).

A carboxylic acid is formed by the oxidation of an aldehyde with the same number of carbon atoms. Because aldehydes are formed from primary alcohols, these alcohols are also a starting material for carboxylic acids.

Carboxylic acids have strong, often disagreeable, odors. They are highly polar molecules and readily engage in hydrogen bonding, so they have relatively high boiling points.

Carboxylic acids are weak acids. They react with bases to form salts and with carbonates and bicarbonates to form carbon dioxide gas and the salt of the acid.

Esters are pleasant-smelling compounds that are responsible for the fragrances of flowers and fruits. They have lower boiling points than comparable carboxylic acids because, even though ester molecules are somewhat polar, they cannot engage in hydrogen bonding. However, with water, esters can engage in hydrogen bonding; consequently, the low molar mass esters are soluble in water. Esters can be synthesized by **esterification**, in which a carboxylic acid and an alcohol are combined under acidic conditions. Esters are neutral compounds that undergo **hydrolysis**, a reaction with water. Under acidic conditions, hydrolysis is essentially the reverse of esterification. When carried out under basic conditions, the process is called **saponification**.

Inorganic acids also react with alcohols to form esters. Some of the most important esters in biochemistry are those formed from phosphoric acid.

Amines are nitrogen-containing organic molecules derived from ammonia ($NH_3$). A **primary (1°) amine** ($RNH_2$) has one organic group bonded to the nitrogen atom, a **secondary (2°) amine** ($R_2NH$) has two organic groups bonded to the nitrogen atom, and a **tertiary (3°) amine** ($R_3N$) has three organic groups bonded to the nitrogen atom. Amines are basic compounds that react with strong acids to produce ammonium ($NH_4^+$) salts. A cyclic compound in which the ring contains one or more noncarbon atoms is called a **heterocyclic compound**. There are many heterocyclic amines, including many physiologically important ones. **Alkaloids** are heterocyclic amines found in many plants. Caffeine, nicotine, and cocaine are familiar alkaloids.

Organic compounds containing a carbonyl group bonded to a nitrogen atom are amides, and the carbon-to-nitrogen bond is an amide linkage (or a peptide linkage). Most amides are colorless and odorless, and the lighter ones are soluble in water. Because they are polar molecules, amides have comparatively high boiling points and melting points. Amides are synthesized from carboxylic acids and $NH_3$ or amines. Amides are neutral compounds. They resist hydrolysis in water, but acids, bases, and enzymes catalyze the reaction.

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# CHAPTER OVERVIEW

## 13: Carbohydrates

Glucose is one of the carbohydrates you will learn about in this chapter as we begin the study of biochemistry—the chemistry of molecules found in living organisms. Later we will study the other three major types of macromolecules found in living organisms: lipids, proteins, and nucleic acids.


- 13.1: Prelude to Carbohydrates
- 13.2: Carbohydrates
- 13.3: Conformations and Stereochemistry
  - 13.3.1: Chirality and stereoisomers
  - 13.3.2: Fischer and Haworth projections
  - 13.3.3: Solutions to Chapter 13.3 exercises
- 13.4: Classes of Monosaccharides
- 13.5: Important Hexoses
- 13.6: Properties of Monosaccharides
- 13.7: Cyclic Structures of Monosaccharides
- 13.8: Disaccharides
- 13.9: Polysaccharides
- 13.S: Carbohydrates (Summary)


Template:HideTOC

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# 13.1: Prelude to Carbohydrates

In the United States, 17.9 million people have been diagnosed with diabetes, and experts estimate that at least another 5.7 million people have the disease but have not been diagnosed. In 2006, diabetes was the seventh leading cause of death, listed on 72,507 death certificates. Moreover, it was a contributing factor in over 200,000 deaths in which the cause was listed as something else, such as heart or kidney disease.

People with diabetes are impaired in their ability to metabolize glucose, a sugar needed by the body for energy; as a result, excessive quantities of glucose accumulate in the blood and the urine. The characteristic symptoms of diabetes are weight loss, constant hunger, extreme thirst, and frequent urination (the kidneys excrete large amounts of water in an attempt to remove the excess sugar from the blood).

An important diagnostic test for diabetes is the oral glucose tolerance test, which measures the level of glucose in blood plasma. A first measurement is made after a fast of at least 8 h, followed by another measurement 2 h after the person drinks a flavored solution of 75 g of glucose dissolved in water. At the second measurement, the glucose plasma level should be no higher than 139 mg/dL. Individuals with a value between 140 and 199 mg/dL are diagnosed with prediabetes, while those with a value of 200 mg/dL or above are diagnosed with diabetes. Following a diagnosis of diabetes a person will need to monitor his or her blood glucose levels daily (or more often) using a glucose meter.



Figure **13.1.1**: Using a Glucose Meter to Test Blood Glucose Level. (Public Domain; Centers for Disease Control and Prevention).

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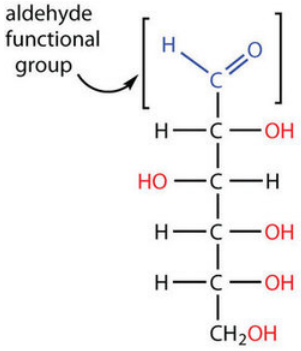
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# 13.2: Carbohydrates

**Learning Objectives**

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

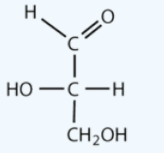
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a "carbon hydrate" with the structure $C_6{\cdot}6H_2O$.

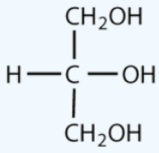


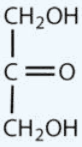

Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

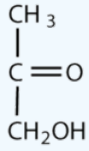
**Example 13.2.1**

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

**Solution**

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.

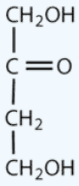
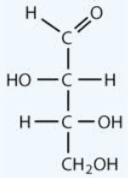
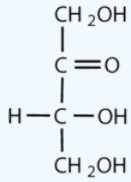
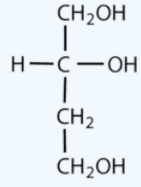
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.

c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

**? Exercise 13.2.1**

Which compounds would be classified as carbohydrates?

1. 
2. 
3. 
4. 

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide ($CO_2$) and water ($H_2O$) by using solar energy in the process known as photosynthesis:

$$6\,CO_2 + 6\,H_2O + 686\text{ kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{13.2.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

> *Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.*

## Summary

Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

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# SECTION OVERVIEW

## 13.3: Conformations and Stereochemistry

Stereochemistry is the study of how bonds are oriented in three-dimensional space. It is difficult to overstate the importance of stereochemistry in nature, and in the fields of biology and medicine in particular. As Pasteur so convincingly demonstrated, life itself is chiral: living things recognize different stereoisomers of organic compounds and process them accordingly.

### 13.3.1: Chirality and stereoisomers

### 13.3.2: Fischer and Haworth projections

### 13.3.3: Solutions to Chapter 13.3 exercises

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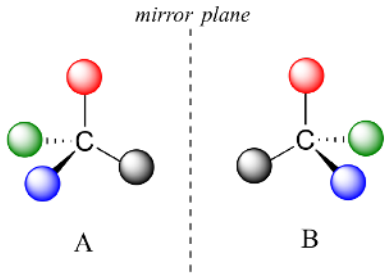
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# 13.3.1: Chirality and stereoisomers

We turn now to concept of chirality, the term **chiral**, from the Greek work for 'hand', refers to anything which cannot be superimposed on its own mirror image. Your hands, of course, are chiral - you cannot superimpose your left hand on your right, and you cannot fit your left hand into a right-handed glove (which is also a chiral object). Another way of saying this is that your hands do not have a **mirror plane of symmetry**: you cannot find any plane which bisects your hand in such a way that one side of the plane is a mirror image of the other side. *Chiral objects do not have a plane of symmetry*.

Your face, on the other hand is **achiral** - lacking chirality - because, some small deviations notwithstanding, you could superimpose your face onto its mirror image. If someone were to show you a mirror image photograph of your face, you could line the image up, point-for-point, with your actual face. Your face has a plane of symmetry, because the left side is the mirror image of the right side.

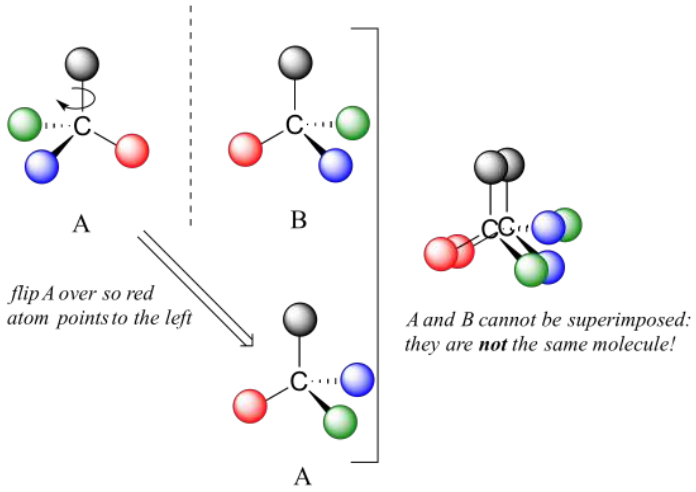
What Pasteur, Biot, and their contemporaries did not yet fully understand when Pasteur made his discovery of molecular chirality was the *source* of chirality at the molecular level. It stood to reason that a chiral molecule is one that does not contain a plane of symmetry, and thus cannot be superimposed on its mirror image. We now know that chiral molecules contain one or more **chiral centers**, which are almost always tetrahedral **carbons with four different substituents**. Consider the cartoon molecule A below: a tetrahedral carbon, with four different substituents denoted by balls of four different colors (for the time being, don't worry about exactly what these substituents could be - we will see real examples very soon).




Another image

The mirror image of A, which we will call B, is drawn on the right side of the figure, and an imaginary mirror is in the middle. Notice that every point on A lines up through the mirror with the same point on B: in other words, if A looked in the mirror, it would see B looking back.

Now, if we flip compound A over and try to superimpose it point for point on compound B, we find that we cannot do it: if we superimpose any two colored balls, then the other two are misaligned.

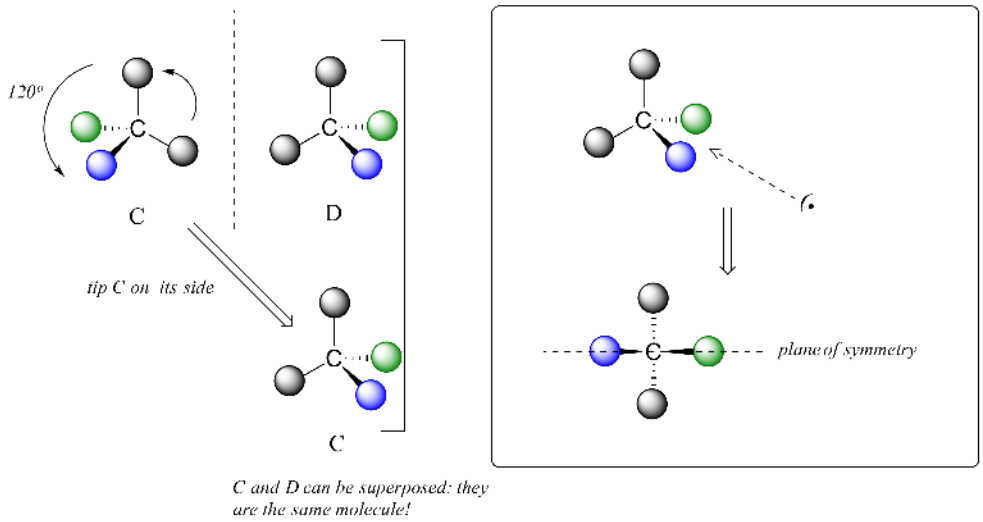



A is not superimposable on its mirror image (B), thus by definition A is a chiral molecule. It follows that B also is not superimposable on *its* mirror image (A), and thus it is also a chiral molecule. Also notice in the figure below (and convince yourself

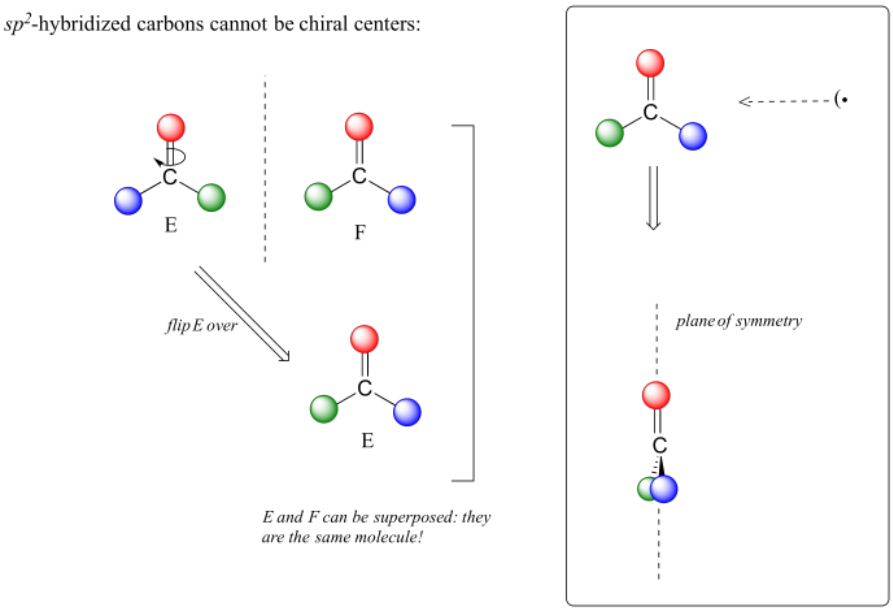
with models) that neither A nor B has an internal plane of symmetry.

A and B are **stereoisomers**: molecules with the same molecular formula and the same bonding arrangement, but *a different arrangement of atoms in space*. There are two types of stereoisomers: enantiomers and diastereomers. **Enantiomers** are pairs of stereoisomers which are mirror images of each other: thus, A and B are enantiomers. It should be self-evident that a chiral molecule will always have one (and *only* one) enantiomer: enantiomers come in pairs. Enantiomers have identical physical properties (melting point, boiling point, density, and so on). However, enantiomers do differ in how they interact with polarized light (we will learn more about this soon) and they may also interact in very different ways with other chiral molecules - proteins, for example. We will begin to explore this last idea in later in this chapter, and see many examples throughout the remainder of our study of biological organic chemistry.

We defined a chiral center as a tetrahedral carbon with four different substituents. If, instead, a tetrahedral carbon has two identical substituents (two black atoms in the cartoon figure below), then of course it still has a mirror image (*everything* has a mirror image). However, it is superimposable on its mirror image, and has a plane of symmetry.




This molecule is **achiral** (lacking chirality). Using the same reasoning, we can see that a trigonal planar carbon is also not a chiral center.



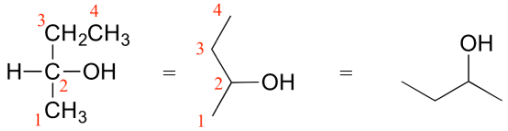


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Notice that structure E can be superimposed on F, its mirror image - all you have to do is pick E up, flip it over, and it is the same as F. This molecule has a plane of symmetry, and is achiral.

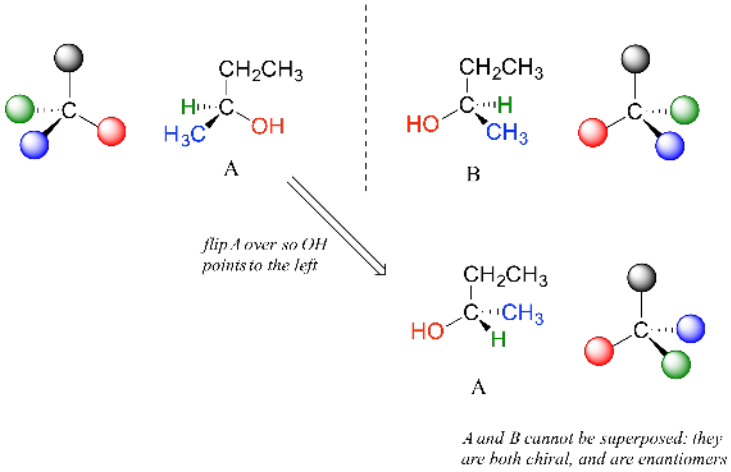
Let's apply our general discussion to real molecules. For now, we will limit our discussion to molecules with a single chiral center. It turns out that tartaric acid, the subject of our chapter introduction, has *two* chiral centers, so we will come back to it later.

Consider 2-butanol, drawn in two dimensions below.



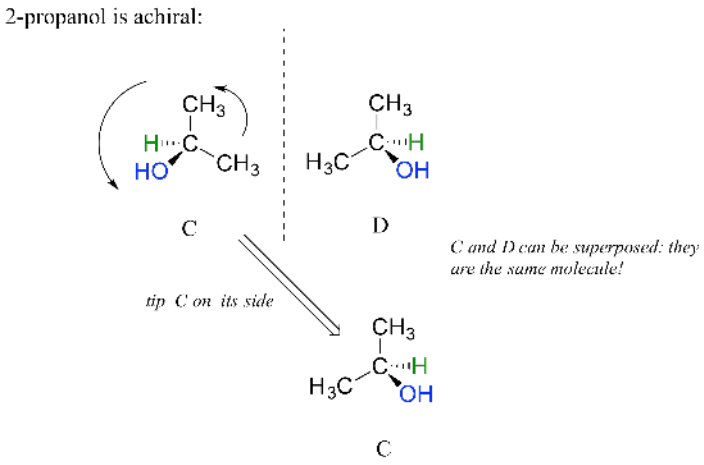

2-butanol
*(drawn in 2D)*

Carbon #2 is a chiral center: it is tetrahedral (even though it is not drawn that way above), and the four things attached to is are different: a hydrogen, a methyl ($-CH_3$) group, an ethyl ($-CH_2CH_3$) group, and a hydroxyl (OH) group. Let's draw the bonding at $C_2$ in three dimensions, and call this structure A. We will also draw the mirror image of A, and call this structure B.




When we try to superimpose A onto B, we find that we cannot do it. A and B are both chiral molecules, and they are enantiomers of each other.

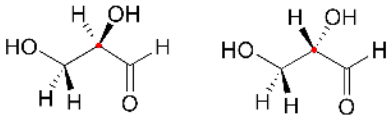
2-propanol, unlike 2-butanol, is *not* a chiral molecule. Carbon #2 is bonded to two identical substituents (methyl groups), and so it is not a chiral center.

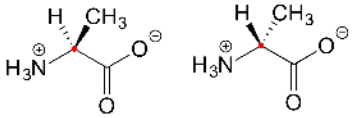


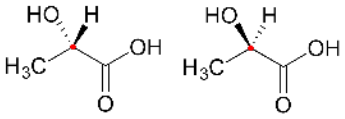

Notice that 2-propanol is superimposable on its own mirror image.

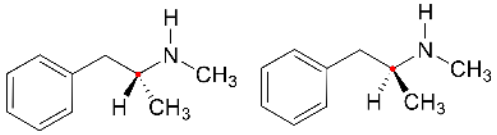
When we look at very simple molecules like 2-butanol, it is not difficult to draw out the mirror image and recognize that it is not superimposable. However, with larger, more complex molecules, this can be a daunting challenge in terms of drawing and three-dimensional visualization. The easy way to determine if a molecule is chiral is simply to look for the presence of one or more chiral centers: molecules with chiral centers will (almost always) be chiral. We insert the 'almost always' caveat here because it is possible to come up with the exception to this rule - we will have more to say on this later, but don't worry about it for now.

Here are four more examples of chiral biomolecules, each one shown as a pair of enantiomers, with chiral centers marked by red dots.

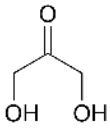

glyceraldehyde

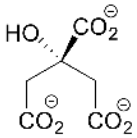

alanine

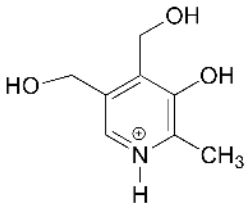

lactic acid

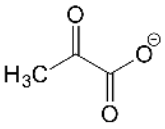

methamphetamine

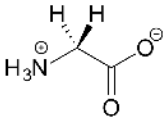
Here are some examples of ***achiral*** biomolecules - convince yourself that none of them contain a chiral center:

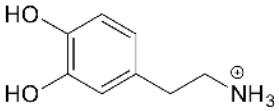

dihydroxyacetone


citrate


pyridoxine
(vitamin $B_6$)

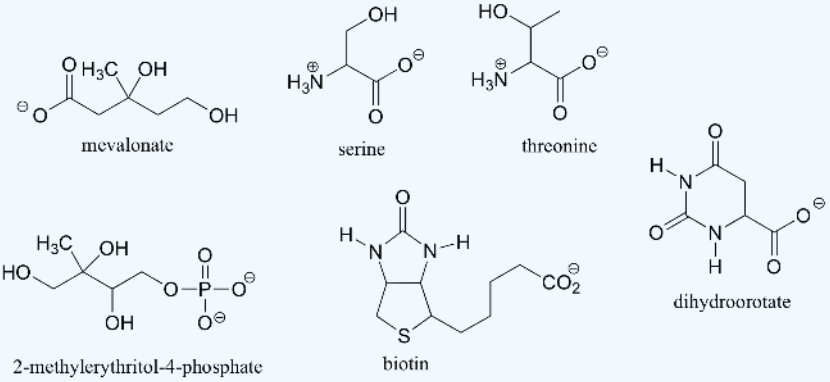

pyruvate


glycine
(amino acid)


dopamine
(neurotransmitter)

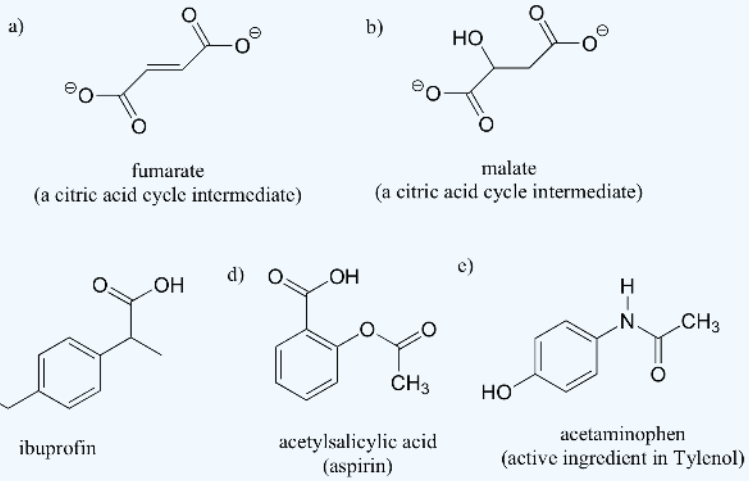
**Exercise 3.8**

Locate all of the chiral centers (there may be more than one in a molecule). Remember, hydrogen atoms bonded to carbon usually are not drawn in the line structure convention - but they are still there!




**Exercise 3.10**

Label the molecules below as chiral or achiral, and locate all chiral centers.




## Khan Academy video tutorials

Chirality

Enantiomers

## Contributors and Attributions

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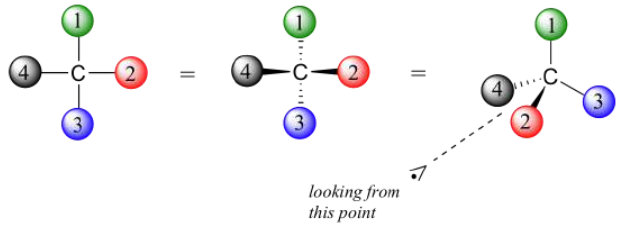
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# 13.3.2: Fischer and Haworth projections

When reading the chemical and biochemical literature, you are likely to encounter several different conventions for drawing molecules in three dimensions, depending on the context of the discussion. While organic chemists prefer to use the dashed/solid wedge convention to show stereochemistry, biochemists often use drawings called **Fischer projections** and **Haworth projections** to discuss and compare the structure of sugar molecules.

Fisher projections show sugars in their open chain form. In a Fischer projection, the carbon atoms of a sugar molecule are connected vertically by solid lines, while carbon-oxygen and carbon-hydrogen bonds are shown horizontally. Stereochemical information is conveyed by a simple rule: vertical bonds point into the plane of the page, while horizontal bonds point out of the page.




Notice that although a Haworth projection is a convenient way to show stereochemistry, it does not provide a realistic depiction of conformation. To show *both* conformation and stereochemistry, you must draw the ring in the chair form, as in structure C above.

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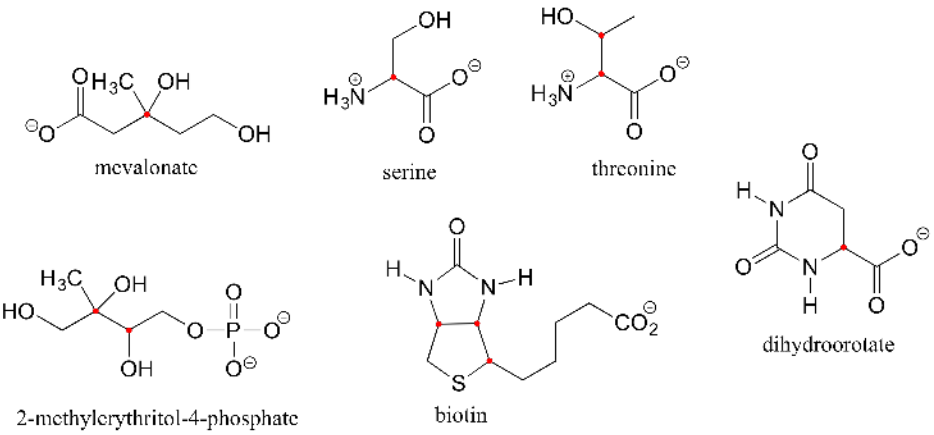
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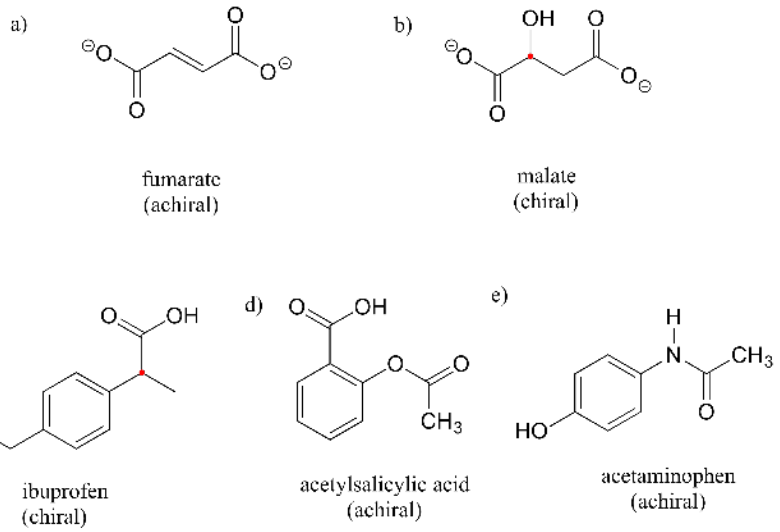
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# 13.3.3: Solutions to Chapter 13.3 exercises

**E3.8**: Chiral centers are designated with a dot.




**E3.10**:




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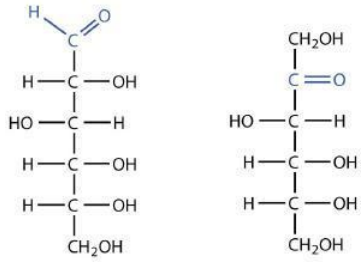
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# 13.4: Classes of Monosaccharides

**Learning Objectives**

- Classify monosaccharides as aldoses or ketoses and as trioses, tetroses, pentoses, or hexoses.
- Distinguish between a D sugar and an L sugar.

The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.



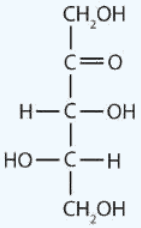

**Example 13.4.1**

Draw an example of each type of compound.

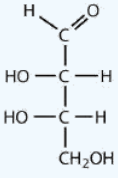
a. a ketopentose
b. an aldotetrose

**Solution**

a. The structure must have five carbon atoms with the second carbon atom being a carbonyl group and the other four carbon atoms each having an OH group attached. Several structures are possible, but one example is shown.



- The structure must have four carbon atoms with the first carbon atom part of the aldehyde functional group. The other three carbon atoms each have an OH group attached. Several structures are possible, but one example is shown.



**? Exercise 13.4.1**

Draw an example of each type of compound.

a. an aldohexose
b. a ketotetrose

The simplest sugars are the trioses. The possible trioses are shown in part (a) of Figure **13.4.1**; glyceraldehyde is an aldotriose, while dihydroxyacetone is a ketotriose. Notice that two structures are shown for glyceraldehyde. These structures are stereoisomers, and hence are isomers having the same structural formula but differing in the arrangement of atoms or groups of atoms in three-dimensional space. If you make models of the two stereoisomers of glyceraldehyde, you will find that you cannot place one model on top of the other and have each functional group point in the same direction. However, if you place one of the models in front of a mirror, the image in the mirror will be identical to the second stereoisomer in part (b) of Figure **13.4.1**. Molecules that are nonsuperimposable (nonidentical) mirror images of each other are a type of stereoisomer called enantiomers (Greek *enantios*, meaning "opposite").

**Note**

These are another type of stereoisomers than the *cis-trans* (geometric) isomers previously discussed.

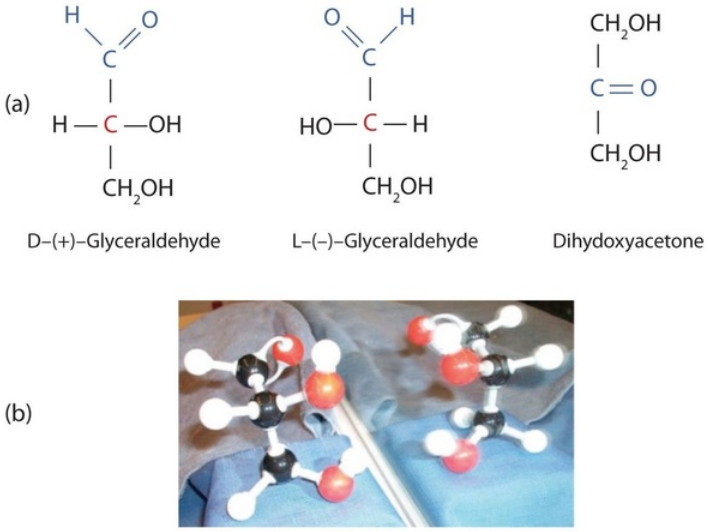



Figure **13.4.1**: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

A key characteristic of enantiomers is that they have a carbon atom to which four different groups are attached. Note, for example, the four different groups attached to the central carbon atom of glyceraldehyde (part (a) of Figure **13.4.1**). A carbon atom that has four different groups attached is a chiral carbon. If a molecule contains one or more chiral carbons, it is likely to exist as two or more stereoisomers. Dihydroxyacetone does not contain a chiral carbon and thus does not exist as a pair of stereoisomers. Glyceraldehyde, however, has a chiral carbon and exists as a pair of enantiomers. Except for the direction in which each enantiomer rotates plane-polarized light, these two molecules have identical physical properties. One enantiomer has a specific rotation of +8.7°, while the other has a specific rotation of −8.7°.

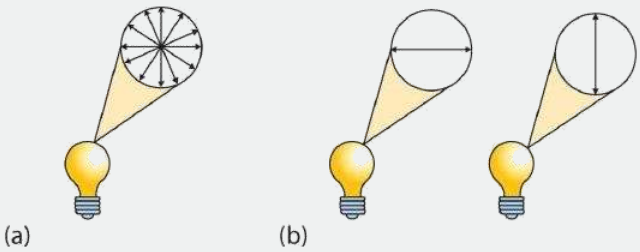
H. Emil Fischer, a German chemist, developed the convention commonly used for writing two-dimensional representations of the monosaccharides, such as those in part (a) of Figure **13.4.1**. In these structural formulas, the aldehyde group is written at the top, and the hydrogen atoms and OH groups that are attached to each chiral carbon are written to the right or left. (If the monosaccharide is a ketose, the ketone functional group is the second carbon atom.) Vertical lines represent bonds pointing away from you, while horizontal lines represent bonds coming toward you. The formulas of chiral molecules represented in this manner are referred to as **Fischer projections**.

The two enantiomers of glyceraldehyde are especially important because monosaccharides with more than three carbon atoms can be considered as being derived from them. Thus, D- and L-glyceraldehyde provide reference points for designating and drawing all other monosaccharides. Sugars whose Fischer projections terminate in the same configuration as D-glyceraldehyde are designated as D sugars; those derived from L-glyceraldehyde are designated as L sugars.

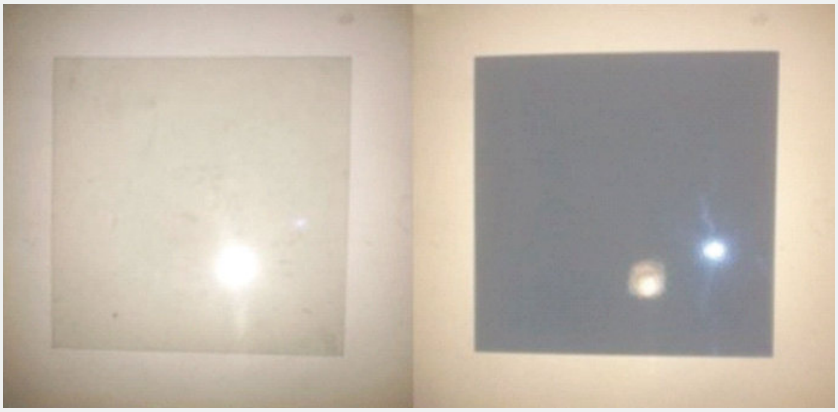
> *By convention, the penultimate (next-to-last) carbon atom has been chosen as the carbon atom that determines if a sugar is D or L. It is the chiral carbon farthest from the aldehyde or ketone functional group.*

### Looking Closer: Polarized Light

A beam of ordinary light can be pictured as a bundle of waves; some move up and down, some sideways, and others at all other conceivable angles. When a beam of light has been polarized, however, the waves in the bundle all vibrate in a single plane. Light altered in this way is called *plane-polarized light*. Much of what chemists know about stereoisomers comes from studying the effects they have on plane-polarized light. In this illustration, the light on the left is not polarized, while that on the right is polarized.




Sunlight, in general, is not polarized; light from an ordinary light bulb or an ordinary flashlight is not polarized. One way to polarize ordinary light is to pass it through Polaroid sheets, special plastic sheets containing carefully oriented organic compounds that permit only light vibrating in a single plane to pass through. To the eye, polarized light doesn't "look" any different from nonpolarized light. We can detect polarized light, however, by using a second sheet of polarizing material, as shown here.



*In the photo on the left, two Polaroid sheets are aligned in the same direction; plane-polarized light from the first Polaroid sheet can pass through the second sheet. In the photo on the right, the top Polaroid sheet has been rotated 90° and now blocks the plane-polarized light that comes through the first Polaroid sheet.*

Certain substances act on polarized light by rotating the plane of vibration. Such substances are said to be optically active. The extent of optical activity is measured by a polarimeter, an instrument that contains two polarizing lenses separated by a sample tube, as shown in the accompanying figure. With the sample tube empty, maximum light reaches the observer's eye when the two lenses are aligned so that both pass light vibrating in the same plane. When an optically active substance is placed in the sample tube, that substance rotates the plane of polarization of the light passing through it, so that the polarized light emerging from the

sample tube is vibrating in a different direction than when it entered the tube. To see the maximum amount of light when the sample is in place, the observer must rotate one lens to accommodate the change in the plane of polarization.

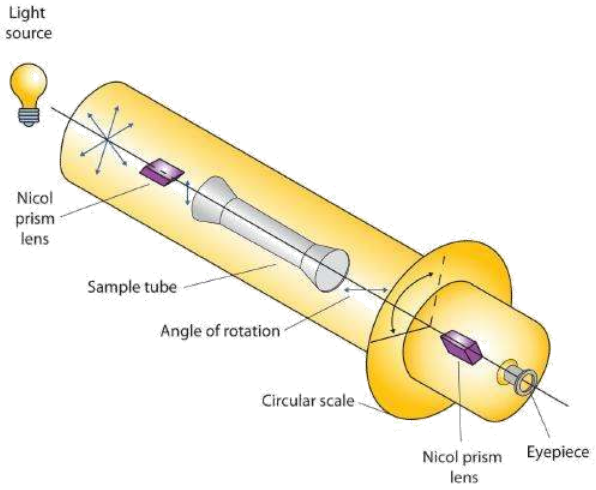



Figure **13.4.2**: Diagram of a Polarimeter

Some optically active substances rotate the plane of polarized light to the right (clockwise) from the observer's point of view. These compounds are said to be dextrorotatory; substances that rotate light to the left (counterclockwise) are levorotatory. To denote the direction of rotation, a positive sign (+) is given to dextrorotatory substances, and a negative sign (−) is given to levorotatory substances.

## Summary

Monosaccharides can be classified by the number of carbon atoms in the structure and/or the type of carbonyl group they contain (aldose or ketose). Most monosaccharides contain at least one chiral carbon and can form stereoisomers. Enantiomers are a specific type of stereoisomers that are mirror images of each other.

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# 13.5: Important Hexoses

**Learning Objectives**

- To identify the structures of D-glucose, D-galactose, and D-fructose and describe how they differ from each other.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 13.5.1). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

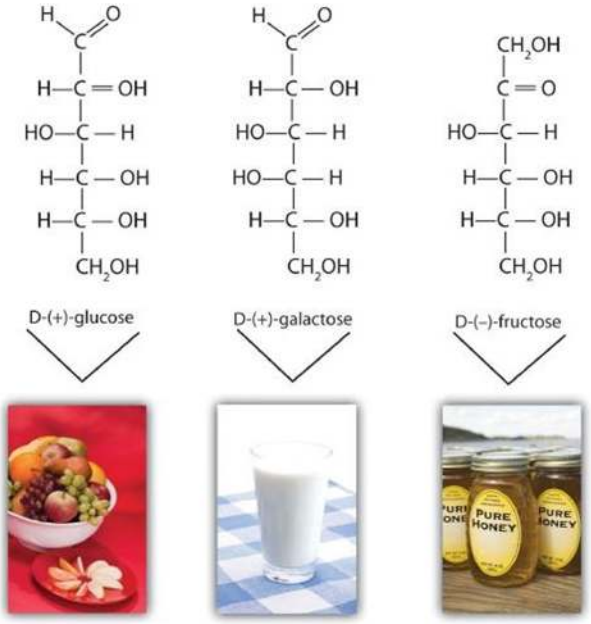



Figure 13.5.1: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

## Glucose

D-Glucose, generally referred to as simply glucose, is the most abundant sugar found in nature; most of the carbohydrates we eat are eventually converted to it in a series of biochemical reactions that produce energy for our cells. It is also known by three other names: *dextrose*, from the fact that it rotates plane-polarized light in a clockwise (dextrorotatory) direction; *corn sugar* because in the United States cornstarch is used in the commercial process that produces glucose from the hydrolysis of starch; and *blood sugar* because it is the carbohydrate found in the circulatory system of animals. Normal blood sugar values range from 70 to 105 mg glucose/dL plasma, and normal urine may contain anywhere from a trace to 20 mg glucose/dL urine.

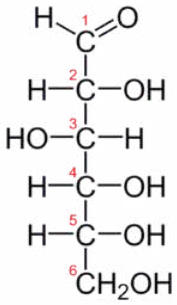


Figure 13.5.2: Fischer projection of D-glucose

The Fischer projection of D-glucose is given in Figure **13.5.2**. Glucose is a D sugar because the OH group on the fifth carbon atom (the chiral center farthest from the carbonyl group) is on the right. In fact, all the OH groups except the one on the third carbon atom are to the right.

## Galactose

D-Galactose does not occur in nature in the uncombined state. It is released when lactose, a disaccharide found in milk, is hydrolyzed. The galactose needed by the human body for the synthesis of lactose is obtained by the metabolic conversion of D-glucose to D-galactose. Galactose is also an important constituent of the glycolipids that occur in the brain and the myelin sheath of nerve cells. For this reason it is also known as *brain sugar*. The structure of D-galactose is shown in Figure **13.5.1**. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

## Fructose

D-Fructose, also shown in Figure **13.5.1**, is the most abundant ketohexose. Note that from the third through the sixth carbon atoms, its structure is the same as that of glucose. It occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. Fructose (from the Latin *fructus*, meaning "fruit") is also referred to as *levulose* because it has a specific rotation that is strongly levorotatory (−92.4°). It is the sweetest sugar, being 1.7 times sweeter than sucrose, although many nonsugars are several hundred or several thousand times as sweet (Table **13.5.1**).

Table **13.5.1**: The Relative Sweetness of Some Compounds (Sucrose = 100)

| Compound | Relative Sweetness |
|---|---|
| lactose | 16 |
| maltose | 32 |
| glucose | 74 |
| sucrose | 100 |
| fructose | 173 |
| aspartame | 18,000 |
| acesulfame K | 20,000 |
| saccharin | 30,000 |
| sucralose | 60,000 |

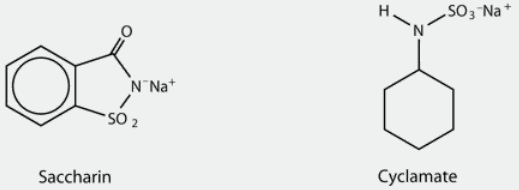
### Looking Closer: Artificial Sweeteners

Although sweetness is commonly associated with mono- and disaccharides, it is not a property found only in sugars. Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake. The synthetic compounds are noncaloric or used in such small quantities that they do not add significantly to the caloric value of food.

The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short years of World War I, the ban was lifted and was not reinstated at the war's end. One drawback to the use of saccharin is its bitter, metallic aftertaste. The initial solution to this problem was to combine saccharin with cyclamate, a second artificial sweetener discovered in 1937.

In the 1960s and 1970s, several clinical tests with laboratory animals implicated both cyclamate and saccharin as carcinogenic (cancer-causing) substances. The results from the cyclamate tests were completed first, and cyclamate was banned in the United States in 1969. Then a major study was released in Canada in 1977 indicating that saccharin increased the incidence of

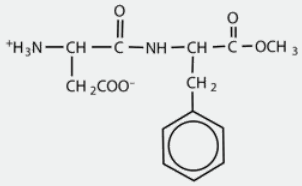
bladder cancer in rats. The US Food and Drug Administration (FDA) proposed a ban on saccharin that raised immediate public opposition because saccharin was the only artificial sweetener still available. In response, Congress passed the Saccharin Study and Labeling Act in 1977, permitting the use of saccharin as long as any product containing it was labeled with a consumer warning regarding the possible elevation of the risk of bladder cancer. Today this warning is no longer required; moreover, the FDA is currently reviewing the ban on cyclamate, as 75 additional studies and years of usage in other countries, such as Canada, have failed to show that it has any carcinogenic effect.



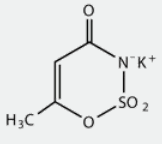

Saccharin



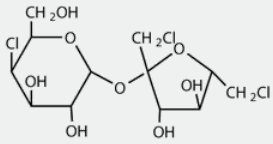

Cyclamate




Aspartame




Acesulfame K




Sucralose

A third artificial sweetener, aspartame, was discovered in 1965. This white crystalline compound is about 180 times sweeter than sucrose and has no aftertaste. It was approved for use in 1981 and is used to sweeten a wide variety of foods because it blends well with other food flavors. Aspartame is not used in baked goods, however, because it is not heat stable.

In the body (or when heated), aspartame is initially hydrolyzed to three molecules: the amino acids aspartic acid and phenylalanine and an alcohol methanol. Repeated controversy regarding the safety of aspartame arises partly from the fact that the body metabolizes the released methanol to formaldehyde. It should be noted, though, that a glass of tomato juice has six times as much methanol as a similar amount of a diet soda containing aspartame. The only documented risk connected to aspartame use is for individuals with the genetic disease *phenylketonuria* (PKU); these individuals lack the enzyme needed to metabolize the phenylalanine released when aspartame is broken down by the body. Because of the danger to people with PKU, all products containing aspartame must carry a warning label.

Acesulfame K, discovered just two years after aspartame (1967), was approved for use in the United States in 1988. It is 200 times sweeter than sugar and, unlike aspartame, is heat stable. It has no lingering aftertaste.

One of the newest artificial sweeteners to gain FDA approval (April 1998) for use in the United States is sucralose, a white crystalline solid approximately 600 times sweeter than sucrose. Sucralose is synthesized from sucrose and has three chlorine atoms substituted for three OH groups. It is noncaloric because it passes through the body unchanged. It can be used in baking because it is heat stable.

All of the extensive clinical studies completed to date have indicated that these artificial sweeteners approved for use in the United States are safe for consumption by healthy individuals in moderate amounts.

## Summary

Three abundant hexoses in living organisms are the aldohexoses D-glucose and D-galactose and the ketohexose D-fructose.

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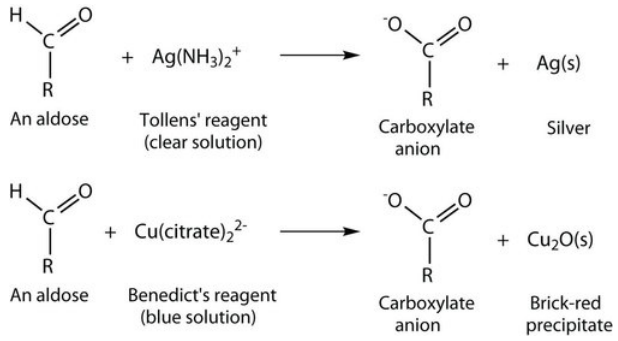
# 13.6: Properties of Monosaccharides

**Learning Objectives**

- To identify the physical and chemical properties of monosaccharides.

Monosaccharides such as glucose and fructose are crystalline solids at room temperature, but they are quite soluble in water, each molecule having several OH groups that readily engage in hydrogen bonding. The chemical behavior of these monosaccharides is likewise determined by their functional groups.

An important reaction of monosaccharides is the oxidation of the aldehyde group, one of the most easily oxidized organic functional groups. Aldehyde oxidation can be accomplished with any mild oxidizing agent, such as Tollens' reagent or Benedict's reagent. With the latter, complexed copper(II) ions are reduced to copper(I) ions that form a brick-red precipitate [copper(I) oxide; Figure **13.6.1**].




Any carbohydrate capable of reducing either Tollens' or Benedict's reagents without first undergoing hydrolysis is said to be a reducing sugar. Because both the Tollens' and Benedict's reagents are basic solutions, ketoses (such as fructose) also give positive tests due to an equilibrium that exists between ketoses and aldoses in a reaction known as *tautomerism*.

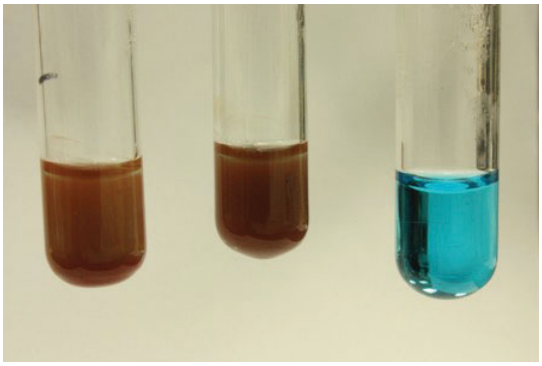


Figure **13.6.1**: Benedict's Test. Benedict's test was performed on three carbohydrates, depicted from left to right: fructose, glucose, and sucrose. The solution containing sucrose remains blue because sucrose is a nonreducing sugar.

These reactions have been used as simple and rapid diagnostic tests for the presence of glucose in blood or urine. For example, Clinitest tablets, which are used to test for sugar in the urine, contain copper(II) ions and are based on Benedict's test. A green color indicates very little sugar, whereas a brick-red color indicates sugar in excess of 2 g/100 mL of urine.

## Summary

Monosaccharides are crystalline solids at room temperature and quite soluble in water. Monosaccharides are reducing sugars; they reduce mild oxidizing agents, such as Tollens' or Benedict's reagents.

## Concept Review Exercises

1. Why are monosaccharides soluble in water?

2. What is a reducing sugar?

## Answers

1. Monosaccharides are quite soluble in water because of the numerous OH groups that readily engage in hydrogen bonding with water.
2. any carbohydrate capable of reducing a mild oxidizing agent, such as Tollens' or Benedict's reagents, without first undergoing hydrolysis

## Exercises

1. Which gives a positive Benedict's test—L-galactose, levulose, or D-glucose?'

Answers

1. All three will give a positive Benedict's test because they are all monosaccharides.

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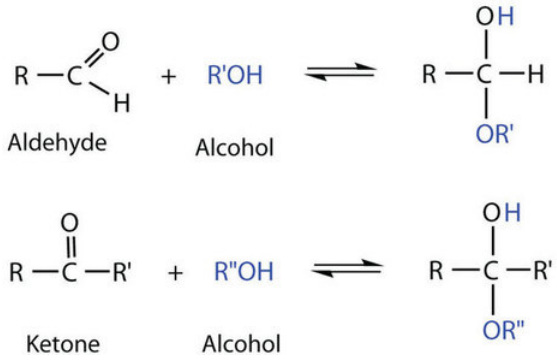
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# 13.7: Cyclic Structures of Monosaccharides

**Learning Objectives**

- Define what is meant by anomers and describe how they are formed.
- Explain what is meant by mutarotation.

So far we have represented monosaccharides as linear molecules, but many of them also adopt cyclic structures. This conversion occurs because of the ability of aldehydes and ketones to react with alcohols:




You might wonder why the aldehyde reacts with the OH group on the fifth carbon atom rather than the OH group on the second carbon atom next to it. Recall that cyclic alkanes containing five or six carbon atoms in the ring are the most stable. The same is true for monosaccharides that form cyclic structures: rings consisting of five or six carbon atoms are the most stable.

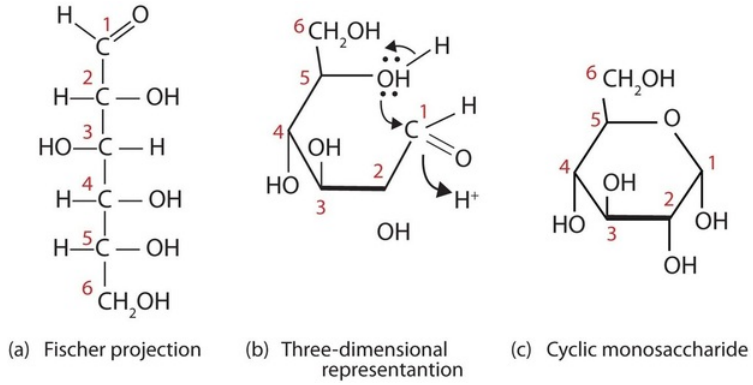



Figure 13.7.1: Cyclization of D-Glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide, such as any of the structures shown in Figure 13.7.1, forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two stereoisomers, as shown in Figure 13.7.2. The structure shown on the left side of Figure 13.7.2, with the OH group on the first carbon atom projected downward, represent what is called the *alpha (α) form*. The structures on the right side, with the OH group on the first carbon atom pointed upward, is the *beta (β) form*. These two stereoisomers of a cyclic monosaccharide are known as anomers; they differ in structure around the anomeric carbon—that is, the carbon atom that was the carbonyl carbon atom in the straight-chain form.

It is possible to obtain a sample of crystalline glucose in which all the molecules have the α structure or all have the β structure. The α form melts at 146°C and has a specific rotation of +112°, while the β form melts at 150°C and has a specific rotation of +18.7°. When the sample is dissolved in water, however, a mixture is soon produced containing both anomers as well as the straight-chain form, in dynamic equilibrium (part (a) of Figure 13.7.2). You can start with a pure crystalline sample of glucose consisting entirely of either anomer, but as soon as the molecules dissolve in water, they open to form the carbonyl group and then reclose to form either the α or the β anomer. The opening and closing repeats continuously in an ongoing interconversion between anomeric forms and is referred to as mutarotation (Latin *mutare*, meaning “to change”). At equilibrium, the mixture consists of

about 36% α-D-glucose, 64% β-D-glucose, and less than 0.02% of the open-chain aldehyde form. The observed rotation of this solution is +52.7°.

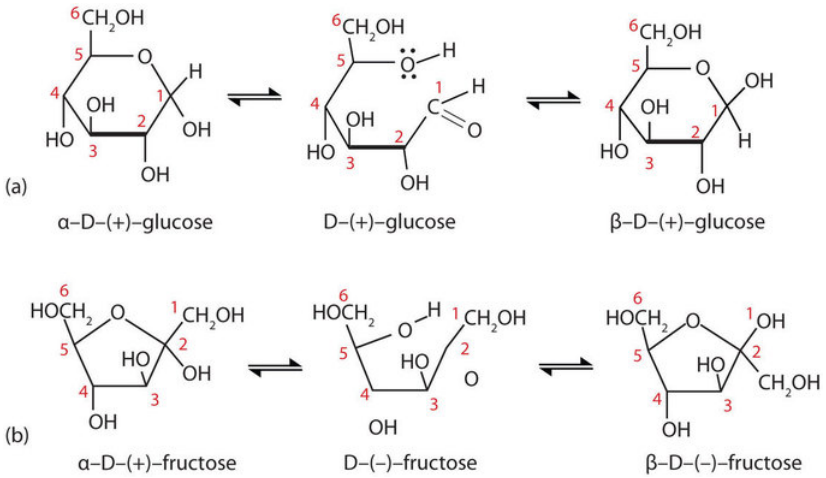



Figure **13.7.2**: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

Even though only a small percentage of the molecules are in the open-chain aldehyde form at any time, the solution will nevertheless exhibit the characteristic reactions of an aldehyde. As the small amount of free aldehyde is used up in a reaction, there is a shift in the equilibrium to yield more aldehyde. Thus, *all* the molecules may eventually react, even though very little free aldehyde is present at a time.

Commonly, (e.g., in Figures **13.7.1** and **13.7.2**) the cyclic forms of sugars are depicted using a convention first suggested by Walter N. Haworth, an English chemist. The molecules are drawn as planar hexagons with a darkened edge representing the side facing toward the viewer. The structure is simplified to show only the functional groups attached to the carbon atoms. Any group written to the right in a Fischer projection appears below the plane of the ring in a Haworth projection, and any group written to the left in a Fischer projection appears above the plane in a Haworth projection.

The difference between the α and the β forms of sugars may seem trivial, but such structural differences are often crucial in biochemical reactions. This explains why we can get energy from the starch in potatoes and other plants but not from cellulose, even though both starch and cellulose are polysaccharides composed of glucose molecules linked together.

## Summary

Monosaccharides that contain five or more carbons atoms form cyclic structures in aqueous solution. Two cyclic stereoisomers can form from each straight-chain monosaccharide; these are known as anomers. In an aqueous solution, an equilibrium mixture forms between the two anomers and the straight-chain structure of a monosaccharide in a process known as mutarotation.

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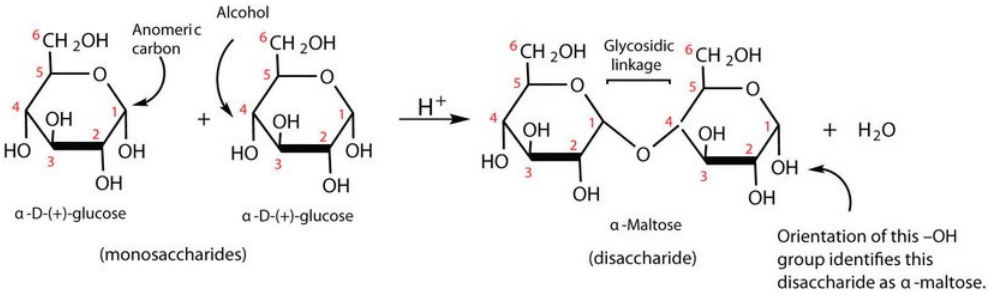
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# 13.8: Disaccharides

**Learning Objectives**

- Identify the structures of sucrose, lactose, and maltose.
- Identify the monosaccharides that are needed to form sucrose, lactose, and maltose

Previously, you learned that monosaccharides can form cyclic structures by the reaction of the carbonyl group with an OH group. These cyclic molecules can in turn react with another alcohol. Disaccharides ($C_{12}H_{22}O_{11}$) are sugars composed of two monosaccharide units that are joined by a carbon–oxygen-carbon linkage known as a glycosidic linkage. This linkage is formed from the reaction of the anomeric carbon of one cyclic monosaccharide with the OH group of a second monosaccharide.




The disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water. We'll consider each sugar in more detail.

## Maltose

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units.

In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*. The same reactions can be carried out in the laboratory with dilute acid as a catalyst, although in that case the rate is much slower, and high temperatures are required. Whether it occurs in the body or a glass beaker, the hydrolysis of maltose produces two molecules of D-glucose.

$$\text{maltose} \xrightarrow{\text{H}^+ \text{ or maltase}} 2\ \text{D-glucose}$$

Maltose is a reducing sugar. Thus, its two glucose molecules must be linked in such a way as to leave one anomeric carbon that can open to form an aldehyde group. The glucose units in maltose are joined in a *head-to-tail* fashion through an α-linkage from the first carbon atom of one glucose molecule to the fourth carbon atom of the second glucose molecule (that is, an α-1,4-glycosidic linkage; see Figure **13.8.1**). The bond from the anomeric carbon of the first monosaccharide unit is directed downward, which is why this is known as an α-glycosidic linkage. The OH group on the anomeric carbon of the second glucose can be in either the α or the β position, as shown in Figure **13.8.1**.

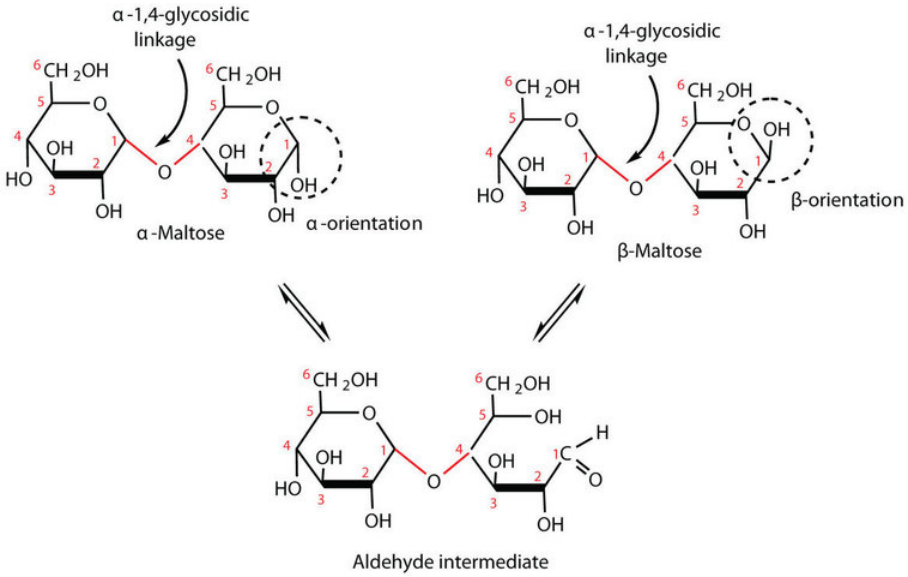
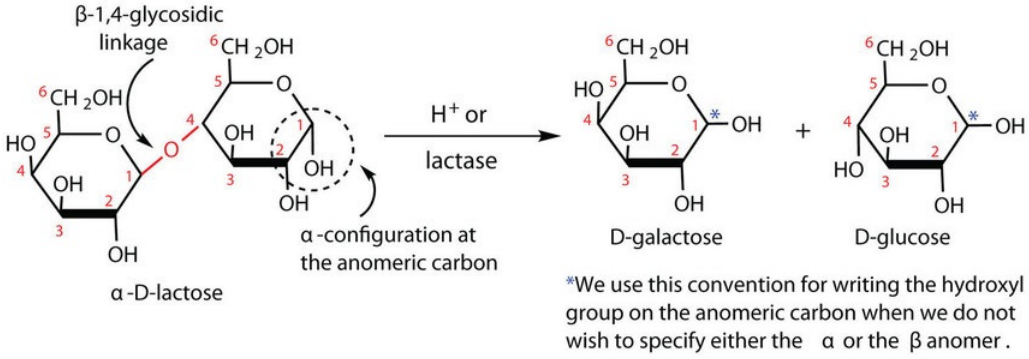



Figure **13.8.1**: An Equilibrium Mixture of Maltose Isomers

## Lactose

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow's milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

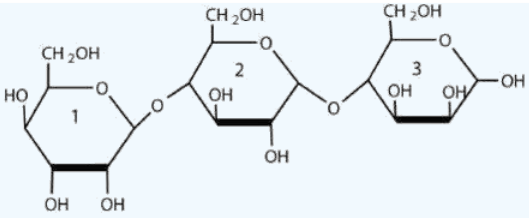
Lactose is a reducing sugar composed of one molecule of D-galactose and one molecule of D-glucose joined by a β-1,4-glycosidic bond (the bond from the anomeric carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic action of the enzyme *lactase*:




Many adults and some children suffer from a deficiency of lactase. These individuals are said to be lactose intolerant because they cannot digest the lactose found in milk. A more serious problem is the genetic disease galactosemia, which results from the absence of an enzyme needed to convert galactose to glucose. Certain bacteria can metabolize lactose, forming lactic acid as one of the products. This reaction is responsible for the "souring" of milk.

**Example 13.8.1**

For this trisaccharide, indicate whether each glycosidic linkage is α or β.

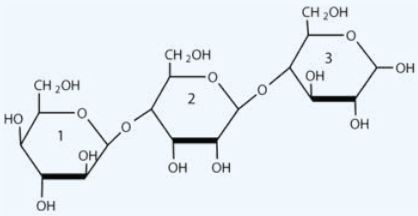


**Solution**

The glycosidic linkage between sugars 1 and 2 is β because the bond is directed up from the anomeric carbon. The glycosidic linkage between sugars 2 and 3 is α because the bond is directed down from the anomeric carbon.

**? Exercise 13.8.1**

For this trisaccharide, indicate whether each glycosidic linkage is α or β.



**To Your Health: Lactose Intolerance and Galactosemia**

Lactose makes up about 40% of an infant's diet during the first year of life. Infants and small children have one form of the enzyme lactase in their small intestines and can digest the sugar easily; however, adults usually have a less active form of the enzyme, and about 70% of the world's adult population has some deficiency in its production. As a result, many adults experience a reduction in the ability to hydrolyze lactose to galactose and glucose in their small intestine. For some people the inability to synthesize sufficient enzyme increases with age. Up to 20% of the US population suffers some degree of lactose intolerance.

In people with lactose intolerance, some of the unhydrolyzed lactose passes into the colon, where it tends to draw water from the interstitial fluid into the intestinal lumen by osmosis. At the same time, intestinal bacteria may act on the lactose to produce organic acids and gases. The buildup of water and bacterial decay products leads to abdominal distention, cramps, and diarrhea, which are symptoms of the condition.

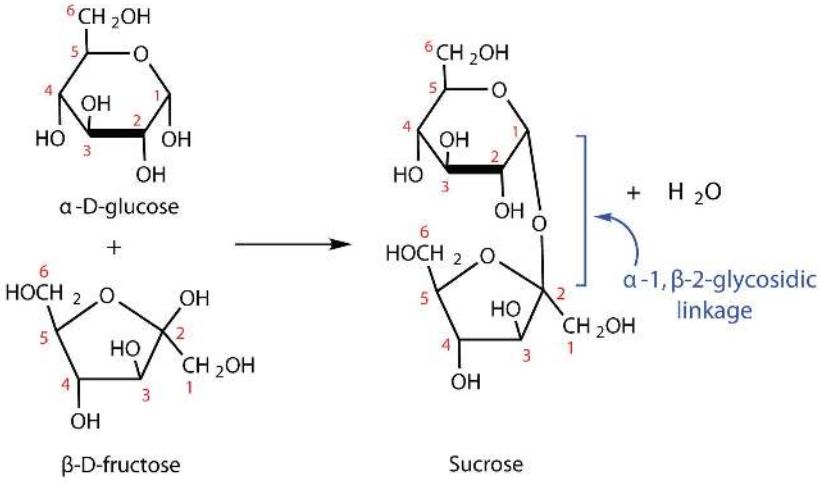
The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis of the lactose, so some people with lactose intolerance are still able to enjoy cheese, yogurt, or cooked foods containing milk. The most common treatment for lactose intolerance, however, is the use of lactase preparations (e.g., Lactaid), which are available in liquid and tablet form at drugstores and grocery stores. These are taken orally with dairy foods—or may be added to them directly—to assist in their digestion.

Galactosemia is a condition in which one of the enzymes needed to convert galactose to glucose is missing. Consequently, the blood galactose level is markedly elevated, and galactose is found in the urine. An infant with galactosemia experiences a lack of appetite, weight loss, diarrhea, and jaundice. The disease may result in impaired liver function, cataracts, mental retardation, and even death. If galactosemia is recognized in early infancy, its effects can be prevented by the exclusion of milk and all other sources of galactose from the diet. As a child with galactosemia grows older, he or she usually develops an alternate pathway for metabolizing galactose, so the need to restrict milk is not permanent. The incidence of galactosemia in the United States is 1 in every 65,000 newborn babies.

## Sucrose

Sucrose, probably the largest-selling pure organic compound in the world, is known as *beet sugar*, *cane sugar*, *table sugar*, or simply *sugar*. Most of the sucrose sold commercially is obtained from sugar cane and sugar beets (whose juices are 14%–20% sucrose) by evaporation of the water and recrystallization. The dark brown liquid that remains after the recrystallization of sugar is sold as molasses.

The sucrose molecule is unique among the common disaccharides in having an α-1,β-2-glycosidic (head-to-head) linkage. Because this glycosidic linkage is formed by the OH group on the anomeric carbon of α-D-glucose and the OH group on the anomeric carbon of β-D-fructose, it ties up the anomeric carbons of both glucose and fructose.




This linkage gives sucrose certain properties that are quite different from those of maltose and lactose. As long as the sucrose molecule remains intact, neither monosaccharide "uncyclizes" to form an open-chain structure. Thus, sucrose is incapable of mutarotation and exists in only one form both in the solid state and in solution. In addition, sucrose does not undergo reactions that are typical of aldehydes and ketones. Therefore, sucrose is a nonreducing sugar.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as invertase) gives an equimolar mixture of glucose and fructose. This 1:1 mixture is referred to as *invert sugar* because it rotates plane-polarized light in the opposite direction than sucrose. The hydrolysis reaction has several practical applications. Sucrose readily recrystallizes from a solution, but invert sugar has a much greater tendency to remain in solution. In the manufacture of jelly and candy and in the canning of fruit, the recrystallization of sugar is undesirable. Therefore, conditions leading to the hydrolysis of sucrose are employed in these processes. Moreover, because fructose is sweeter than sucrose, the hydrolysis adds to the sweetening effect. Bees carry out this reaction when they make honey.

The average American consumes more than 100 lb of sucrose every year. About two-thirds of this amount is ingested in soft drinks, presweetened cereals, and other highly processed foods. The widespread use of sucrose is a contributing factor to obesity and tooth decay. Carbohydrates such as sucrose, are converted to fat when the caloric intake exceeds the body's requirements, and sucrose causes tooth decay by promoting the formation of plaque that sticks to teeth.

## Summary

Maltose is composed of two molecules of glucose joined by an α-1,4-glycosidic linkage. It is a reducing sugar that is found in sprouting grain. Lactose is composed of a molecule of galactose joined to a molecule of glucose by a β-1,4-glycosidic linkage. It is a reducing sugar that is found in milk. Sucrose is composed of a molecule of glucose joined to a molecule of fructose by an α-1,β-2-glycosidic linkage. It is a nonreducing sugar that is found in sugar cane and sugar beets

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# 13.9: Polysaccharides

**Learning Objectives**

- To compare and contrast the structures and uses of starch, glycogen, and cellulose.

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

## Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. We often think of potatoes as a "starchy" food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (part (a) of Figure **13.9.1**). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure **13.9.1**). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

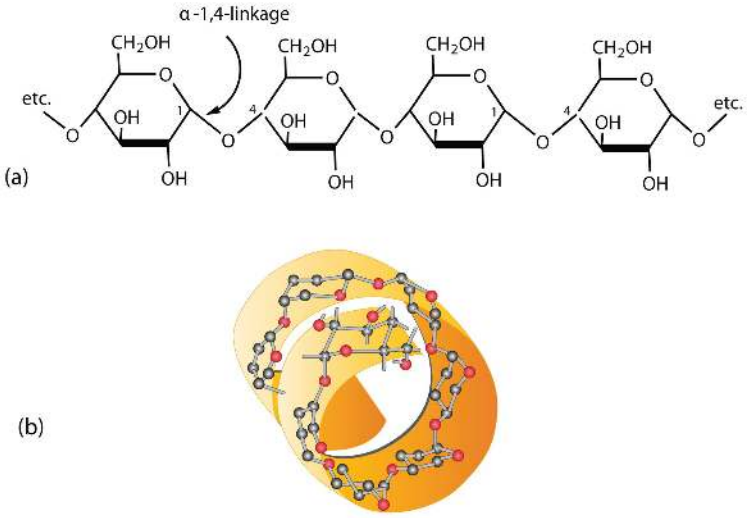



Figure **13.9.1**: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure **13.9.2**). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

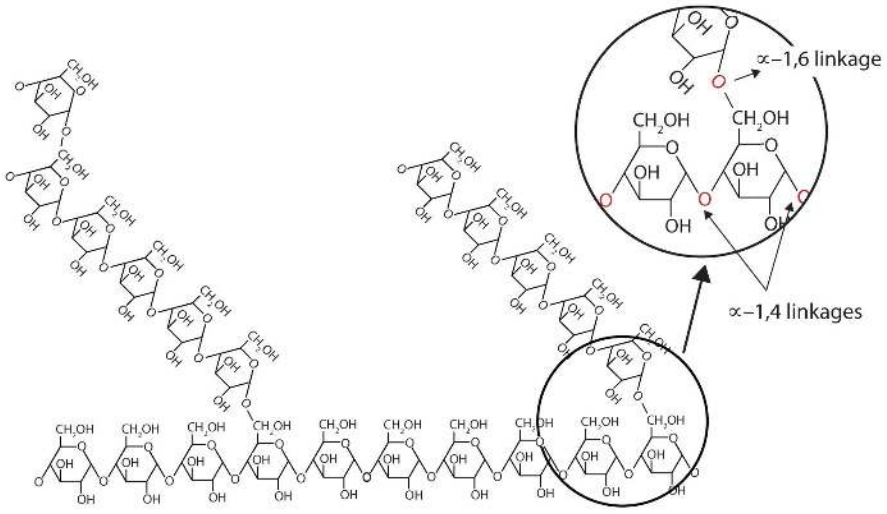



Figure **13.9.2**: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

## Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

> *About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.*

## Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure **13.9.3**). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure **13.9.3**). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

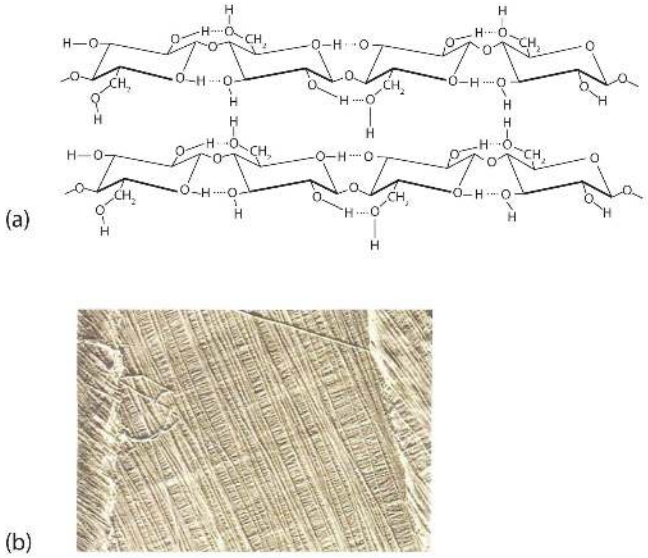



Figure **13.9.3**: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

## Career Focus: Certified Diabetes Educator

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.



A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

> Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

## Summary

Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched). Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin. Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β-1,4-glycosidic bonds.

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# 13.S: Carbohydrates (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

**Carbohydrates**, a large group of biological compounds containing carbon, hydrogen, and oxygen atoms, include sugars, starch, glycogen, and cellulose. All carbohydrates contain alcohol functional groups, and either an aldehyde or a ketone group (or a functional group that can be converted to an aldehyde or ketone). The simplest carbohydrates are **monosaccharides**. Those with two monosaccharide units are **disaccharides**, and those with many monosaccharide units are **polysaccharides**. Most sugars are either monosaccharides or disaccharides. Cellulose, glycogen, and starch are polysaccharides.

Many carbohydrates exist as **stereoisomers**, in which the three-dimensional spatial arrangement of the atoms in space is the only difference between the isomers. These particular stereoisomers contain at least one **chiral carbon**, a carbon atom that has four different groups bonded to it. A molecule containing a chiral carbon is nonsuperimposable on its mirror image, and two molecules that are nonsuperimposable mirror images of each other are a special type of stereoisomer called **enantiomers**. Enantiomers have the same physical properties, such as melting point, but differ in the direction they rotate polarized light.

A sugar is designated as being a D sugar or an L sugar according to how, in a Fischer projection of the molecule, the hydrogen atom and OH group are attached to the *penultimate* carbon atom, which is the carbon atom immediately before the terminal alcohol carbon atom. If the structure at this carbon atom is the same as that of D-glyceraldehyde (OH to the right), the sugar is a **D sugar**; if the configuration is the same as that of L-glyceraldehyde (OH to the left), the sugar is an **L sugar**.

Monosaccharides of five or more carbons atoms readily form cyclic structures when the carbonyl carbon atom reacts with an OH group on a carbon atom three or four carbon atoms distant. Consequently, glucose in solution exists as an equilibrium mixture of three forms, two of them cyclic (α- and β-) and one open chain. In Haworth projections, the *alpha* form is drawn with the OH group on the "former" carbonyl carbon atom (**anomeric carbon**) pointing downward; the *beta* form, with the OH group pointing upward; these two compounds are stereoisomers and are given the more specific term of **anomers**. Any solid sugar can be all alpha or all beta. Once the sample is dissolved in water, however, the ring opens up into the open-chain structure and then closes to form either the α- or the β-anomer. These interconversions occur back and forth until a dynamic equilibrium mixture is achieved in a process called **mutarotation**.

The carbonyl group present in monosaccharides is easily oxidized by Tollens' or Benedict's reagents (as well as others). Any mono- or disaccharide containing a free anomeric carbon is a **reducing sugar**. The disaccharide *maltose* contains two glucose units joined in an α-1,4-glycosidic linkage. The disaccharide *lactose* contains a galactose unit and a glucose unit joined by a β-1,4-glycosidic linkage. Both maltose and lactose contain a free anomeric carbon that can convert to an aldehyde functional group, so they are reducing sugars; they also undergo mutarotation. Many adults, and some children, have a deficiency of the enzyme lactase (which is needed to break down lactose) and are said to be **lactose intolerant**. A more serious problem is the genetic disease **galactosemia**, which results from the absence of an enzyme needed to convert galactose to glucose.

The disaccharide *sucrose* (table sugar) consists of a glucose unit and a fructose unit joined by a glycosidic linkage. The linkage is designated as an α-1,β-2-glycosidic linkage because it involves the OH group on the first carbon atom of glucose and the OH group on the second carbon atom of fructose. Sucrose is not a reducing sugar because it has no anomeric carbon that can reform a carbonyl group, and it cannot undergo mutarotation because of the restrictions imposed by this linkage.

*Starch*, the principal carbohydrate of plants, is composed of the polysaccharides **amylose** (10%–30%) and **amylopectin** (70%–90%). When ingested by humans and other animals, starch is hydrolyzed to glucose and becomes the body's energy source. *Glycogen* is the polysaccharide animals use to store excess carbohydrates from their diets. Similar in structure to amylopectin, glycogen is hydrolyzed to glucose whenever an animal needs energy for a metabolic process. The polysaccharide *cellulose* provides structure for plant cells. It is a linear polymer of glucose units joined by β-1,4-glycosidic linkages. It is indigestible in the human body but digestible by many microorganisms, including microorganisms found in the digestive tracts of many herbivores.

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# CHAPTER OVERVIEW

## 14: Lipids

The lipids are a large and diverse group of naturally occurring organic compounds that are related by their solubility in nonpolar organic solvents (e.g., ether, chloroform, acetone and benzene) and general insolubility in water. There is great structural variety among the lipids, as will be demonstrated in the following sections.


14.1: Prelude to Lipids
14.2: Fatty Acids
14.3: Fats and Oils
14.4: Steroids
14.5: Membranes and Membrane Lipids
14.E: Exercises
14.S: Lipids (Summary)


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# 14.1: Prelude to Lipids

On July 11, 2003, the Food and Drug Administration amended its food labeling regulations to require that manufacturers list the amount of *trans* fatty acids on Nutrition Facts labels of foods and dietary supplements, effective January 1, 2006. This amendment was a response to published studies demonstrating a link between the consumption of *trans* fatty acids and an increased risk of heart disease. *Trans* fatty acids are produced in the conversion of liquid oils to solid fats, as in the creation of many commercial margarines and shortenings. They have been shown to increase the levels of low-density lipoproteins (LDLs)—complexes that are often referred to as bad cholesterol—in the blood. In this chapter, you will learn about fatty acids and what is meant by a *trans* fatty acid, as well as the difference between fats and oils. You will also learn what cholesterol is and why it is an important molecule in the human body.

Fats and oils, found in many of the foods we eat, belong to a class of biomolecules known as lipids. Gram for gram, they pack more than twice the caloric content of carbohydrates: the oxidation of fats and oils supplies about 9 kcal of energy for every gram oxidized, whereas the oxidation of carbohydrates supplies only 4 kcal/g. Although the high caloric content of fats may be bad news for the dieter, it says something about the efficiency of nature's designs. Our bodies use carbohydrates, primarily in the form of glucose, for our *immediate* energy needs. Our capacity for storing carbohydrates for later use is limited to tucking away a bit of glycogen in the liver or in muscle tissue. We store our *reserve* energy in lipid form, which requires far less space than the same amount of energy stored in carbohydrate form. Lipids have other biological functions besides energy storage. They are a major component of the membranes of the 10 trillion cells in our bodies. They serve as protective padding and insulation for vital organs. Furthermore, without lipids in our diets, we would be deficient in the fat-soluble vitamins A, D, E, and K.

Lipids are not defined by the presence of specific functional groups, as carbohydrates are, but by a physical property—solubility. Compounds isolated from body tissues are classified as lipids if they are more soluble in organic solvents, such as dichloromethane, than in water. By this criterion, the lipid category includes not only fats and oils, which are esters of the trihydroxy alcohol glycerol and fatty acids, but also compounds that incorporate functional groups derived from phosphoric acid, carbohydrates, or amino alcohols, as well as steroid compounds such as cholesterol (Figure **14.1.1** presents one scheme for classifying the various kinds of lipids). We will discuss the various kinds of lipids by considering one subclass at a time and pointing out structural similarities and differences as we go.

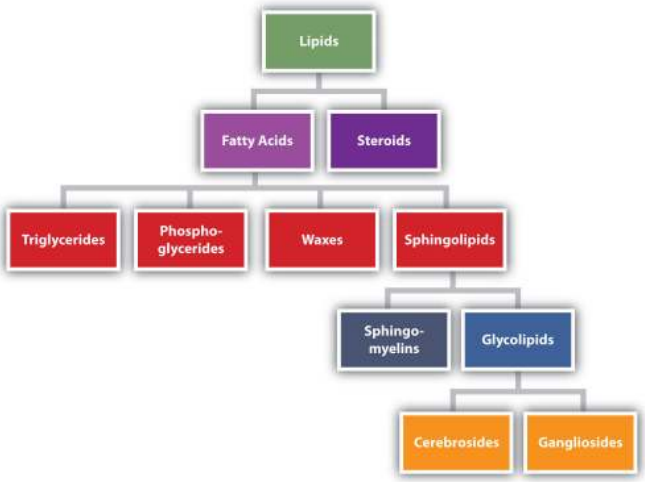



Figure **14.1.1**: Lipid Organization Based on Structural Relationships

Lipid categorized into fatty acids and steroids. Fatty acids are further separated into triglycerides, phospho-glycerides, waxes, and sphingolipids. Sphingolipids are separated into sphingo-myelins and glycolipids. Glycolipids are separated into cerebrosides and gangliosides.

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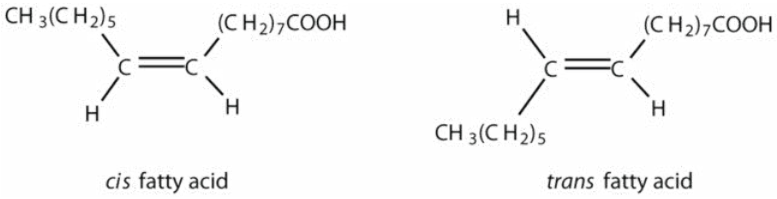
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# 14.2: Fatty Acids

**Learning Objectives**

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.




Cis fatty acids have two H atoms on the same side of the plane of the fatty acid while trans has the two H atoms on opposite sides.

Table **14.2.1** lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the cis or trans isomeric form. Naturally occurring fatty acids are generally in the cis configuration.

Table **14.2.1**: Some Common Fatty Acids Found in Natural Fats

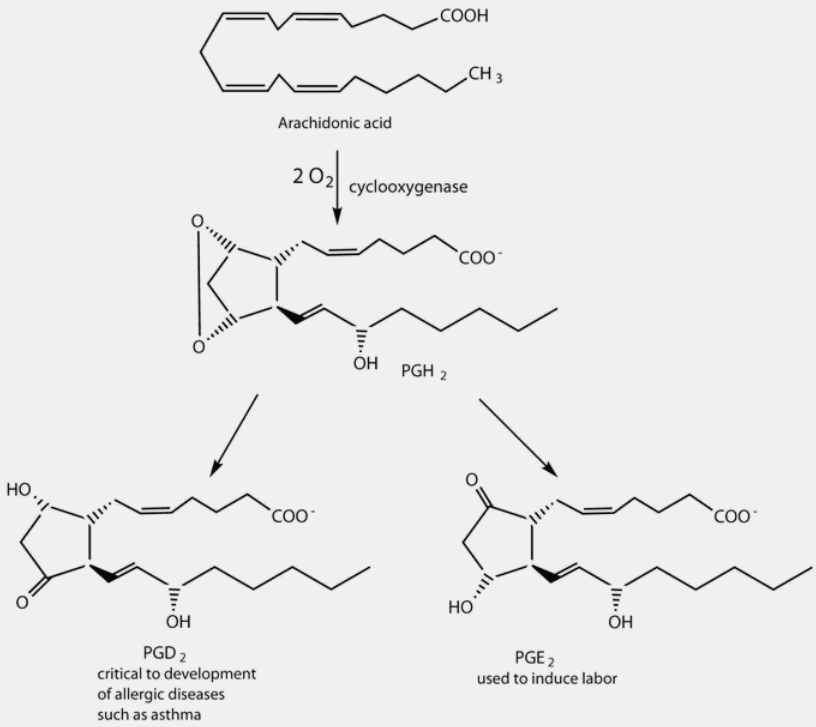
| Name | Abbreviated Structural Formula | Condensed Structural Formula | Melting Point (°C) | Source |
|---|---|---|---|---|
| lauric acid | $C_{11}H_{23}COOH$ | $CH_3(CH_2)_{10}COOH$ | 44 | palm kernel oil |
| myristic acid | $C_{13}H_{27}COOH$ | $CH_3(CH_2)_{12}COOH$ | 58 | oil of nutmeg |
| palmitic acid | $C_{15}H_{31}COOH$ | $CH_3(CH_2)_{14}COOH$ | 63 | palm oil |
| palmitoleic acid | $C_{15}H_{29}COOH$ | $CH_3(CH_2)_5CH=CH(CH_2)_7COOH$ | 0.5 | macadamia oil |
| stearic acid | $C_{17}H_{35}COOH$ | $CH_3(CH_2)_{16}COOH$ | 70 | cocoa butter |
| oleic acid | $C_{17}H_{33}COOH$ | $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ | 16 | olive oil |
| linoleic acid | $C_{17}H_{31}COOH$ | $CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$ | −5 | canola oil |
| α-linolenic acid | $C_{17}H_{29}COOH$ | $CH_3(CH_2CH=CH)_3(CH_2)_7COOH$ | −11 | flaxseed |
| arachidonic acid | $C_{19}H_{31}COOH$ | $CH_3(CH_2)_4(CH_2CH=CH)_4(CH_2)_2COOH$ | −50 | liver |

Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

## To Your Health: Prostaglandins

Prostaglandins are chemical messengers synthesized in the cells in which their physiological activity is expressed. They are unsaturated fatty acids containing 20 carbon atoms and are synthesized from arachidonic acid—a polyunsaturated fatty acid—when needed by a particular cell. They are called *prostaglandins* because they were originally isolated from semen found in the prostate gland. It is now known that they are synthesized in nearly all mammalian tissues and affect almost all organs in the body. The five major classes of prostaglandins are designated as PGA, PGB, PGE, PGF, and PGI. Subscripts are attached at the end of these abbreviations to denote the number of double bonds outside the five-carbon ring in a given prostaglandin.

The prostaglandins are among the most potent biological substances known. Slight structural differences give them highly distinct biological effects; however, all prostaglandins exhibit some ability to induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response. Aspirin and other nonsteroidal anti-inflammatory agents, such as ibuprofen, obstruct the synthesis of prostaglandins by inhibiting cyclooxygenase, the enzyme needed for the initial step in the conversion of arachidonic acid to prostaglandins.




Their wide range of physiological activity has led to the synthesis of hundreds of prostaglandins and their analogs. Derivatives of $PGE_2$ are now used in the United States to induce labor. Other prostaglandins have been employed clinically to lower or increase blood pressure, inhibit stomach secretions, relieve nasal congestion, relieve asthma, and prevent the formation of blood clots, which are associated with heart attacks and strokes.

Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure **14.2.2*a***). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure **14.2.2*b***). Such molecules pack closely together into a crystal lattice, maximizing the strength of dispersion forces and causing fatty acids and the fats derived from them to have relatively high melting points. In contrast, each *cis* carbon-to-carbon double bond in an unsaturated fatty acid produces a pronounced bend in the molecule, so that these molecules do not stack neatly. As a result, the intermolecular attractions of unsaturated fatty acids (and unsaturated fats) are weaker, causing these substances to have lower melting points. Most are liquids at room temperature.

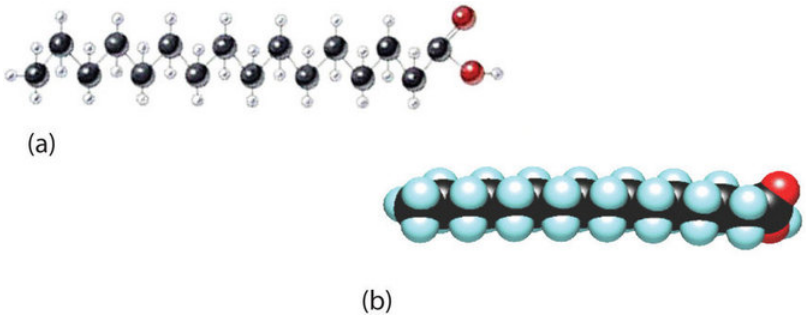
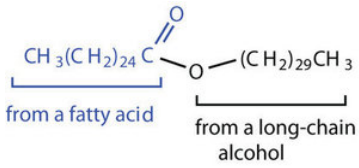



Figure **14.2.2**: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

*Waxes* are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.




Myricyl cerotate
(found in carnauba wax)

## Summary

Fatty acids are carboxylic acids that are the structural components of many lipids. They may be saturated or unsaturated. Most fatty acids are unbranched and contain an even number of carbon atoms. Unsaturated fatty acids have lower melting points than saturated fatty acids containing the same number of carbon atoms.

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# 14.3: Fats and Oils

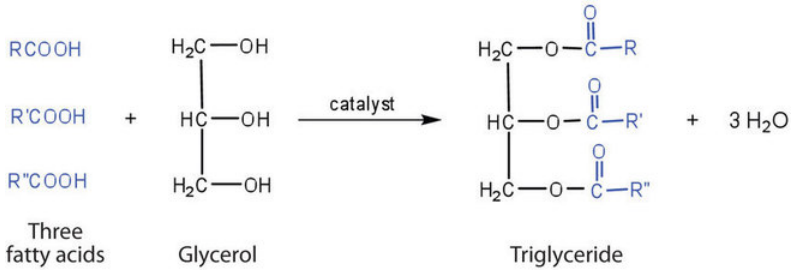
**Learning Objectives**

- Explain why fats and oils are referred to as triglycerides.
- Explain how the fatty acid composition of the triglycerides determines whether a substance is a fat or oil.
- Describe the importance of key reactions of triglycerides, such as hydrolysis, hydrogenation, and oxidation.

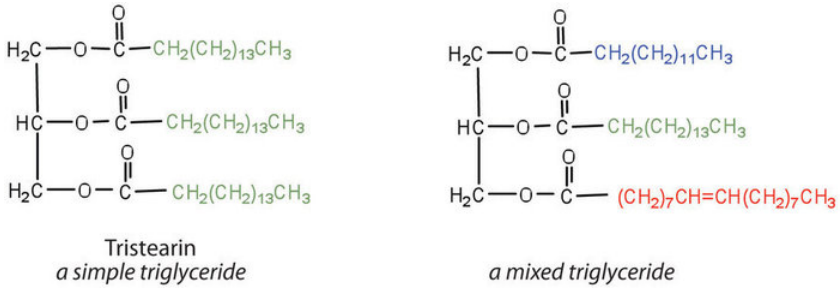
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

## Structures of Fats and Oils

Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:




If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.




A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table **14.3.1** shows the fatty acid compositions of some common fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from as well as on dietetic and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid.

Table **14.3.1**: Average Fatty Acid Composition of Some Common Fats and Oils (%)*

| | Lauric | Myristic | Palmitic | Stearic | Oleic | Linoleic | Linolenic |
|---|---|---|---|---|---|---|---|
| ***Fats*** | | | | | | | |
| butter (cow) | 3 | 11 | 27 | 12 | 29 | 2 | 1 |
| tallow | | 3 | 24 | 19 | 43 | 3 | 1 |
| lard | | 2 | 26 | 14 | 44 | 10 | |
| ***Oils*** | | | | | | | |
| canola oil | | | 4 | 2 | 62 | 22 | 10 |
| coconut oil† | 47 | 18 | 9 | 3 | 6 | 2 | |
| corn oil | | | 11 | 2 | 28 | 58 | 1 |
| olive oil | | | 13 | 3 | 71 | 10 | 1 |
| peanut oil | | | 11 | 2 | 48 | 32 | |
| soybean oil | | | 11 | 4 | 24 | 54 | 7 |

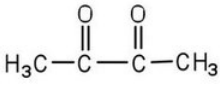
*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

†Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting $C_8$, $C_{10}$, and $C_{12}$ saturated fatty acids.

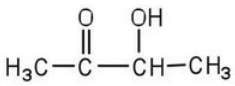
Terms such as *saturated fat* or *unsaturated oil* are often used to describe the fats or oils obtained from foods. Saturated fats contain a high proportion of saturated fatty acids, while unsaturated oils contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

- ## Physical Properties of Fats and Oils

  Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.



Diacetyl

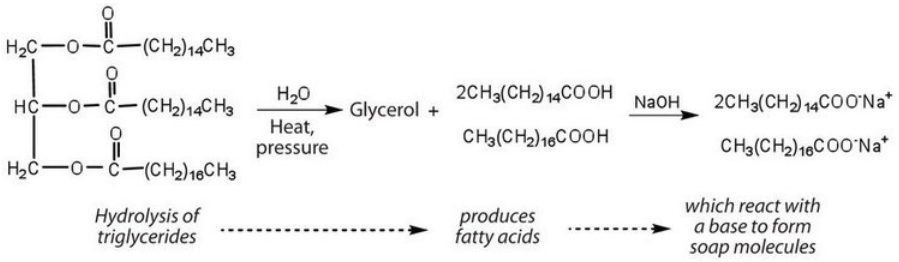


3-hydroxy-2-butanone

  Fats and oils are lighter than water, having densities of about 0.8 g/cm$^3$. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

## Chemical Reactions of Fats and Oils

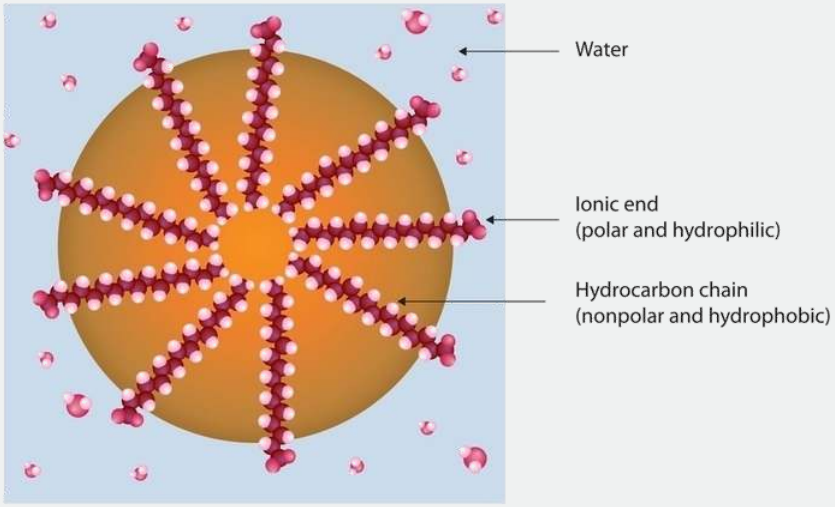
Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in$^2$ (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):




## Looking Closer: Soaps

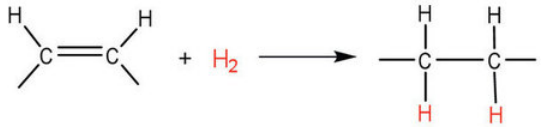
Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.




Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. The droplets repel each other because of their charged surfaces and do not coalesce. With the oil no longer "gluing" the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.

The double bonds in fats and oils can undergo hydrogenation and also oxidation. The hydrogenation of vegetable oils to produce semisolid fats is an important process in the food industry. Chemically, it is essentially identical to the catalytic hydrogenation reaction described for alkenes.



In commercial processes, the number of double bonds that are hydrogenated is carefully controlled to produce fats with the desired consistency (soft and pliable). Inexpensive and abundant vegetable oils (canola, corn, soybean) are thus transformed into margarine and cooking fats. In the preparation of margarine, for example, partially hydrogenated oils are mixed with water, salt, and nonfat dry milk, along with flavoring agents, coloring agents, and vitamins A and D, which are added to approximate the look, taste, and nutrition of butter. (Preservatives and antioxidants are also added.) In most commercial peanut butter, the peanut oil has been partially hydrogenated to prevent it from separating out. Consumers could decrease the amount of saturated fat in their diet by using the original unprocessed oils on their foods, but most people would rather spread margarine on their toast than pour oil on it.

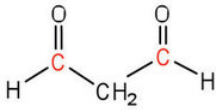
Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* fatty acids mentioned in the opening essay. However, studies have shown that *trans* fatty acids also raise cholesterol levels and increase the incidence of heart disease. *Trans* fatty acids do not have the bend in their structures, which occurs in *cis* fatty acids and thus pack closely together in the same way that the saturated fatty acids do. Consumers are now being advised to use polyunsaturated oils and soft or liquid margarine and reduce their total fat consumption to less than 30% of their total calorie intake each day.

Fats and oils that are in contact with moist air at room temperature eventually undergo oxidation and hydrolysis reactions that cause them to turn rancid, acquiring a characteristic disagreeable odor. One cause of the odor is the release of volatile fatty acids by hydrolysis of the ester bonds. Butter, for example, releases foul-smelling butyric, caprylic, and capric acids. Microorganisms present in the air furnish lipases that catalyze this process. Hydrolytic rancidity can easily be prevented by covering the fat or oil and keeping it in a refrigerator.

Another cause of volatile, odorous compounds is the oxidation of the unsaturated fatty acid components, particularly the readily oxidized structural unit



in polyunsaturated fatty acids, such as linoleic and linolenic acids. One particularly offensive product, formed by the oxidative cleavage of both double bonds in this unit, is a compound called *malonaldehyde*.



Malonaldehyde

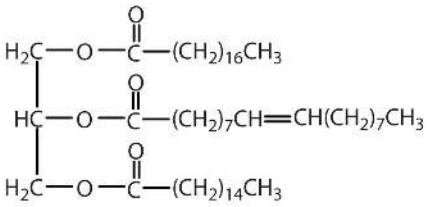
Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better antioxidants, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids.

## Summary

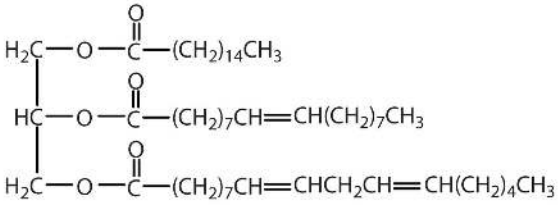
Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol. An increase in the percentage of shorter-chain fatty acids and/or unsaturated fatty acids lowers the melting point of a fat or oil. The hydrolysis of fats and oils in the presence of a base makes soap and is known as saponification. Double bonds present in unsaturated triglycerides can be hydrogenated to convert oils (liquid) into margarine (solid). The oxidation of fatty acids can form compounds with disagreeable odors. This oxidation can be minimized by the addition of antioxidants.

## Concept Review Exercises

1. What functions does fat serve in the body?
2. Which of these triglycerides would you expect to find in higher amounts in oils? In fats? Justify your choice.



(a)



(b)

## Answers

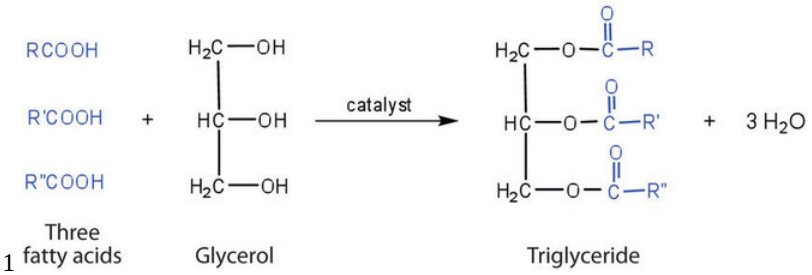
1. Fats provide energy for living organisms. They also provide insulation for body organs and transport fat-soluble vitamins.
2. The triglyceride on the left is expected to be present in higher amounts in fats because it is composed of a greater number of saturated fatty acids. The triglyceride on the right is expected to be present in higher amounts in oils because it is composed of a greater number of unsaturated fatty acids.

## Exercises

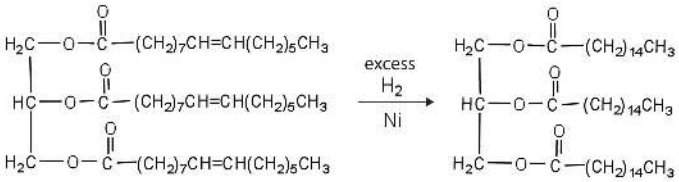
1. Draw the structure for each compound.
   a. trimyristin
   b. a triglyceride likely to be found in peanut oil
2. Draw the structure for each compound.
   a. tripalmitin
   b. a triglyceride likely to be found in butter
3. Draw structures to write the reaction for the complete hydrogenation of tripalmitolein (Use Table 14.2.1 for the condensed structure of palmitoleic acid).
4. Draw structures to write the reaction for the complete hydrogenation of trilinolein (Use Table 14.2.1 for the condensed structure of linoleic acid).
5. Draw structures to write the reaction for the hydrolysis of trilaurin in a basic solution (Use Table 14.2.1 for the condensed structure of lauric acid).
6. Draw structures to write the reaction for the hydrolysis of tristearin in a basic solution (Use Table 14.2.1 for the condensed structure of stearic acid).
7. a. What compounds with a disagreeable odor are formed when butter becomes rancid?
   b. How are these compounds formed?
   c. How can rancidity be prevented?
8. a. What compound with a disagreeable odor is formed when unsaturated fatty acids react with oxygen in the atmosphere?
   b. How can this process be prevented?

## Answers

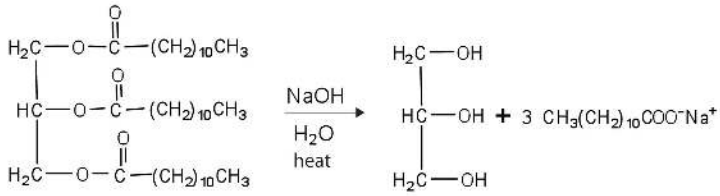
1




3.




5.




7. a. smaller carboxylic acids, such as butyric, caprylic, and capric acids
   b. These compounds are formed by the hydrolysis of the triglycerides found in butter.
   c. Rancidity can be prevented by covering the butter (to keep out moisture) and storing it in a refrigerator. (Cold temperatures slow down hydrolysis reactions.)

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# 14.4: Steroids

**Learning Objectives**

- To identify the functions of steroids produced in mammals.

All the lipids discussed so far are *saponifiable*, reacting with aqueous alkali to yield simpler components, such as glycerol, fatty acids, amino alcohols, and sugars. Lipid samples extracted from cellular material, however, also contain a small but important fraction that does not react with alkali. The most important nonsaponifiable lipids are the steroids. These compounds include the *bile salts*, *cholesterol* and related compounds, and certain *hormones* (such as cortisone and the sex hormones).

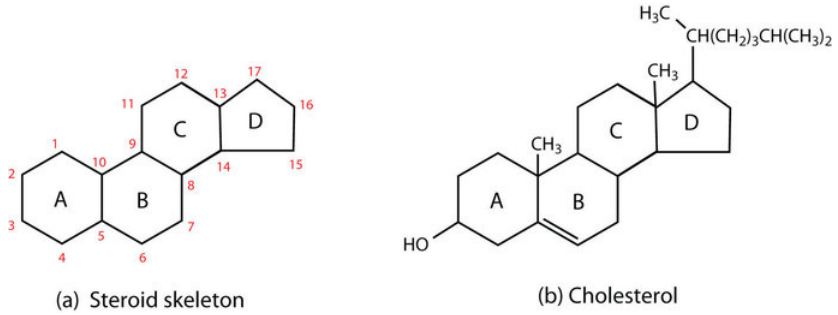



Figure **14.4.1** Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

Steroids occur in plants, animals, yeasts, and molds but not in bacteria. They may exist in free form or combined with fatty acids or carbohydrates. All steroids have a characteristic structural component consisting of four fused rings. Chemists identify the rings by capital letters and number the carbon atoms as shown in Figure **14.4.1***a*. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

## Cholesterol

Cholesterol (Figure **14.4.1***b*) does not occur in plants, but it is the most abundant steroid in the human body (240 g is a typical amount). Excess cholesterol is believed to be a primary factor in the development of atherosclerosis and heart disease, which are major health problems in the United States today. About half of the body's cholesterol is interspersed in the lipid bilayer of cell membranes. Much of the rest is converted to cholic acid, which is used in the formation of bile salts. Cholesterol is also a precursor in the synthesis of sex hormones, adrenal hormones, and vitamin D.

Excess cholesterol not metabolized by the body is released from the liver and transported by the blood to the gallbladder. Normally, it stays in solution there until being secreted into the intestine (as a component of bile) to be eliminated. Sometimes, however, cholesterol in the gallbladder precipitates in the form of gallstones (Figure **14.4.2**). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



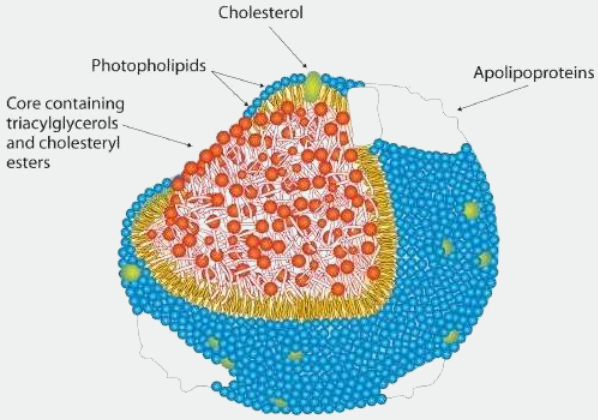
Figure **14.4.2**: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

## To Your Health: Cholesterol and Heart Disease

Heart disease is the leading cause of death in the United States for both men and women. The Centers for Disease Control and Prevention reported that heart disease claimed 631,636 lives in the United States (26% of all reported deaths) in 2006.

Scientists agree that elevated cholesterol levels in the blood, as well as high blood pressure, obesity, diabetes, and cigarette smoking, are associated with an increased risk of heart disease. A long-term investigation by the National Institutes of Health showed that among men ages 30 to 49, the incidence of heart disease was five times greater for those whose cholesterol levels were above 260 mg/100 mL of serum than for those with cholesterol levels of 200 mg/100 mL or less. The cholesterol content of blood varies considerably with age, diet, and sex. Young adults average about 170 mg of cholesterol per 100 mL of blood, whereas males at age 55 may have cholesterol levels at 250 mg/100 mL or higher because the rate of cholesterol breakdown decreases with age. Females tend to have lower blood cholesterol levels than males.

To understand the link between heart disease and cholesterol levels, it is important to understand how cholesterol and other lipids are transported in the body. Lipids, such as cholesterol, are not soluble in water and therefore cannot be transported in the blood (an aqueous medium) unless they are complexed with proteins that are soluble in water, forming assemblages called *lipoproteins*. Lipoproteins are classified according to their density, which is dependent on the relative amounts of protein and lipid they contain. Lipids are less dense than proteins, so lipoproteins containing a greater proportion of lipid are less dense than those containing a greater proportion of protein.




Research on cholesterol and its role in heart disease has focused on serum levels of low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs). One of the most fascinating discoveries is that high levels of HDLs reduce a person's risk of developing heart disease, whereas high levels of LDLs increase that risk. Thus the serum LDL:HDL ratio is a better predictor of heart disease risk than the overall level of serum cholesterol. Persons who, because of hereditary or dietary factors, have high LDL:HDL ratios in their blood have a higher incidence of heart disease.

How do HDLs reduce the risk of developing heart disease? No one knows for sure, but one role of HDLs appears to be the transport of excess cholesterol to the liver, where it can be metabolized. Therefore, HDLs aid in removing cholesterol from blood and from the smooth muscle cells of the arterial wall.

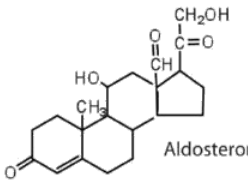
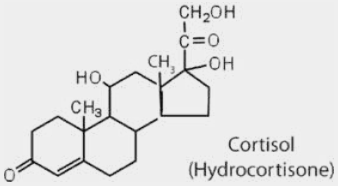
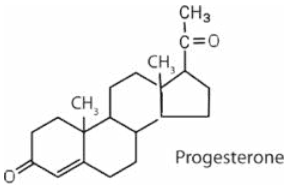
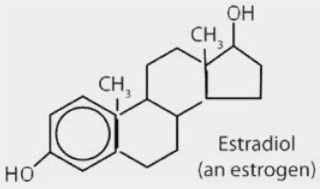
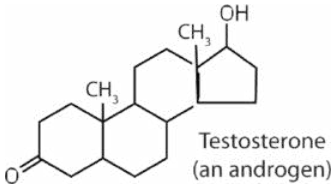
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount of cholesterol synthesized is controlled by the cholesterol level in the blood; when the blood cholesterol level exceeds 150 mg/100 mL, the rate of cholesterol biosynthesis is halved. Hence, if cholesterol is present in the diet, a feedback mechanism suppresses its synthesis in the liver. However, the ratio of suppression is not a 1:1 ratio; the reduction in biosynthesis does not equal the amount of cholesterol ingested. Thus, dietary substitutions of unsaturated fat for saturated fat, as well as a reduction in consumption of *trans* fatty acids, is recommended to help lower serum cholesterol and the risk of heart disease.

## Steroid Hormones

*Hormones* are chemical messengers that are released in one tissue and transported through the circulatory system to one or more other tissues. One group of hormones is known as steroid hormones because these hormones are synthesized from cholesterol, which is also a steroid. There are two main groups of steroid hormones: adrenocortical hormones and sex hormones.

The adrenocortical hormones, such as aldosterone and cortisol (Table **14.4.1**), are produced by the adrenal gland, which is located adjacent to each kidney. Aldosterone acts on most cells in the body, but it is particularly effective at enhancing the rate of reabsorption of sodium ions in the kidney tubules and increasing the secretion of potassium ions and/or hydrogen ions by the tubules. Because the concentration of sodium ions is the major factor influencing water retention in tissues, aldosterone promotes water retention and reduces urine output. Cortisol regulates several key metabolic reactions (for example, increasing glucose production and mobilizing fatty acids and amino acids). It also inhibits the inflammatory response of tissue to injury or stress. Cortisol and its analogs are therefore used pharmacologically as immunosuppressants after transplant operations and in the treatment of severe skin allergies and autoimmune diseases, such as rheumatoid arthritis.

Table **14.4.1**: Representative Steroid Hormones and Their Physiological Effects

| Hormone | Effect |
|---|---|
|  Aldosterone | regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium |
|  Cortisol (Hydrocortisone) | stimulates the conversion of proteins to carbohydrates |
|  Progesterone | regulates the menstrual cycle; maintains pregnancy |
|  Estradiol (an estrogen) | stimulates female sex characteristics; regulates changes during the menstrual cycle |
|  Testosterone (an androgen) | stimulates and maintains male sex characteristics |

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. Testosterone and androstenedione are the primary male sex hormones, or *androgens*, controlling the primary sexual characteristics of males, or the development of the male genital organs and the continuous production of sperm. Androgens are also responsible for the development of secondary male characteristics, such as facial hair, deep voice, and muscle strength. Two kinds of sex

hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estrogens, which are mainly responsible for the development of female secondary sexual characteristics, such as breast development and increased deposition of fat tissue in the breasts, the buttocks, and the thighs. Both males and females produce androgens and estrogens, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other.

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

## Bile Salts

**Bile** is a yellowish green liquid (pH 7.8–8.6) produced in the liver. The most important constituents of bile are bile salts, which are sodium salts of amidelike combinations of bile acids, such as cholic acid (part (a) of Figure **14.4.3**) and an amine such as the amino acid glycine (part (b) of Figure **14.4.3**). They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine. In the gallbladder, the composition of bile gradually changes as water is absorbed and the other components become more concentrated.

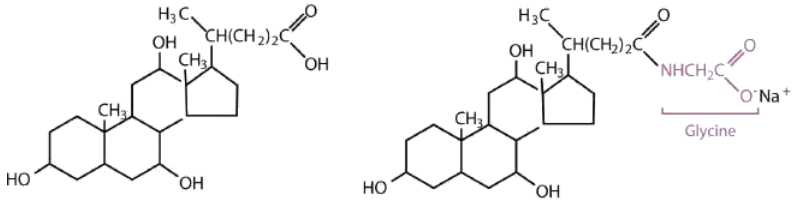



Figure **14.4.3** Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

Because they contain both hydrophobic and hydrophilic groups, bile salts are highly effective detergents and emulsifying agents; they break down large fat globules into smaller ones and keep those smaller globules suspended in the aqueous digestive environment. Enzymes can then hydrolyze fat molecules more efficiently. Thus, the major function of bile salts is to aid in the digestion of dietary lipids.

> Surgical removal is often advised for a gallbladder that becomes infected, inflamed, or perforated. This surgery does not seriously affect digestion because bile is still produced by the liver, but the liver's bile is more dilute and its secretion into the small intestine is not as closely tied to the arrival of food.

## Summary

Steroids have a four-fused-ring structure and have a variety of functions. Cholesterol is a steroid found in mammals that is needed for the formation of cell membranes, bile acids, and several hormones. Bile salts are secreted into the small intestine to aid in the digestion of fats.

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# 14.5: Membranes and Membrane Lipids

**Learning Objectives**

- Identify the distinguishing characteristics of membrane lipids.
- Describe membrane components and how they are arranged.

All living cells are surrounded by a cell membrane. Plant cells (Figure **14.5.1*A***) and animal cells (Figure **14.5.1*B***) contain a cell nucleus that is also surrounded by a membrane and holds the genetic information for the cell. Everything between the cell membrane and the nuclear membrane—including intracellular fluids and various subcellular components such as the mitochondria and ribosomes—is called the cytoplasm. The membranes of all cells have a fundamentally similar structure, but membrane function varies tremendously from one organism to another and even from one cell to another within a single organism. This diversity arises mainly from the presence of different proteins and lipids in the membrane.

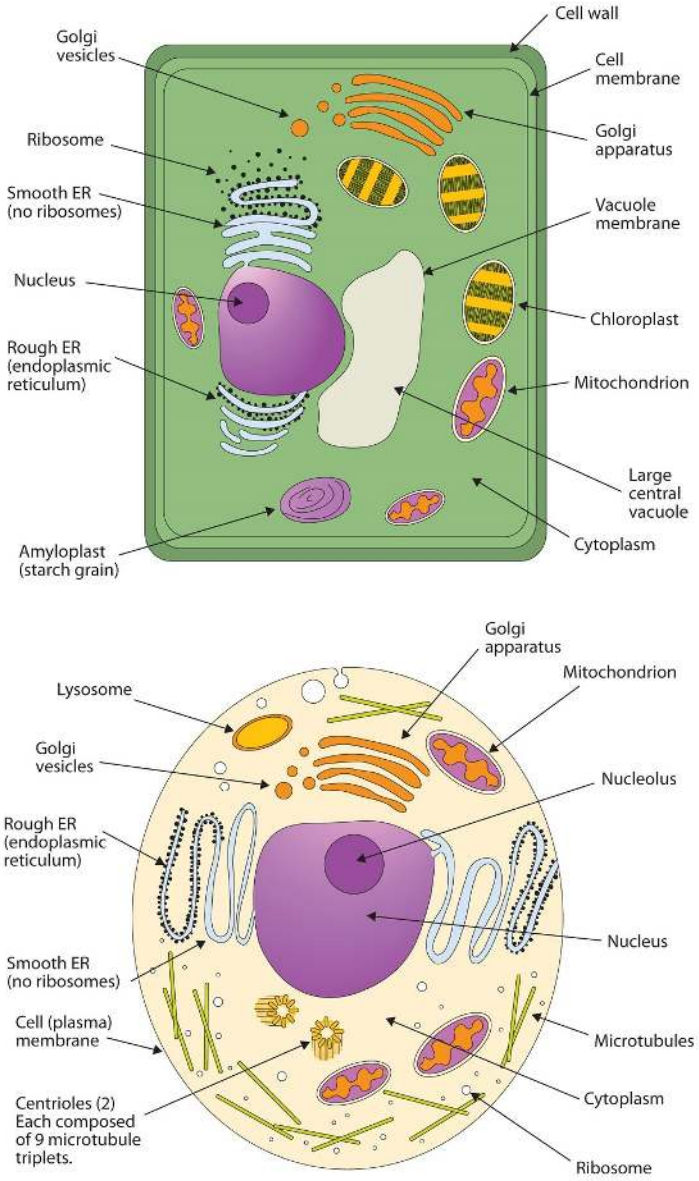



Figure **14.5.1**: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

The lipids in cell membranes are highly polar but have dual characteristics: part of the lipid is ionic and therefore dissolves in water, whereas the rest has a hydrocarbon structure and therefore dissolves in nonpolar substances. Often, the ionic part is referred to as hydrophilic, meaning “water loving,” and the nonpolar part as hydrophobic, meaning “water fearing” (repelled by water). When allowed to float freely in water, polar lipids spontaneously cluster together in any one of three arrangements: micelles, monolayers, and bilayers (Figure **14.5.2**).

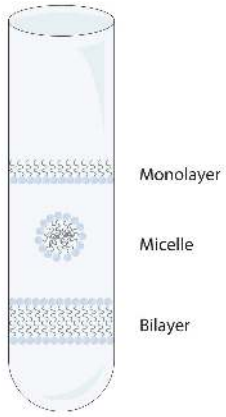



Figure **14.5.2**: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

Micelles are aggregations in which the lipids’ hydrocarbon tails—being hydrophobic—are directed toward the center of the assemblage and away from the surrounding water while the hydrophilic heads are directed outward, in contact with the water. Each micelle may contain thousands of lipid molecules. Polar lipids may also form a monolayer, a layer one molecule thick on the surface of the water. The polar heads face into water, and the nonpolar tails stick up into the air. Bilayers are double layers of lipids arranged so that the hydrophobic tails are sandwiched between an inner surface and an outer surface consisting of hydrophilic heads. The hydrophilic heads are in contact with water on either side of the bilayer, whereas the tails, sequestered inside the bilayer, are prevented from having contact with the water. Bilayers like this make up every cell membrane (Figure **14.5.3**).

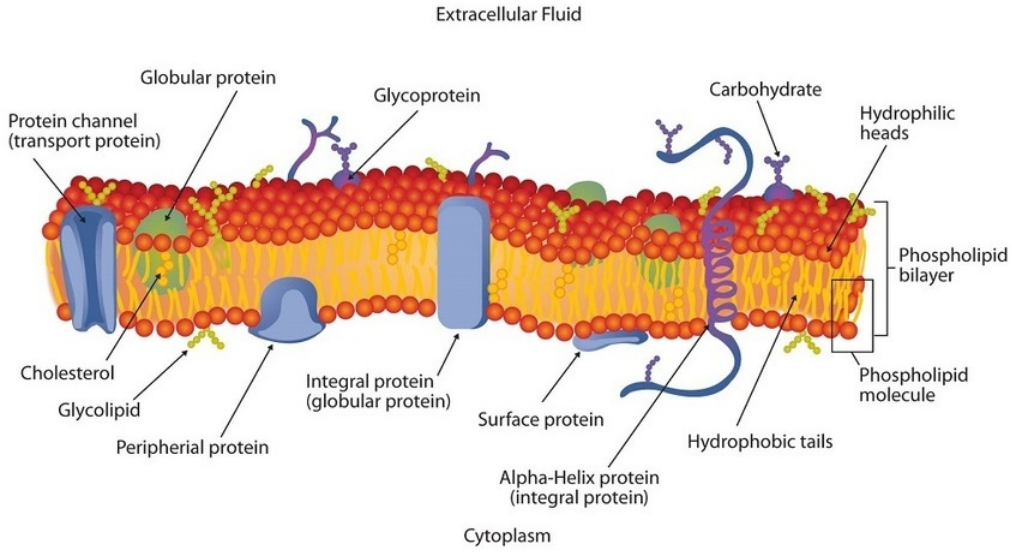



Figure **14.5.3**: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

In the bilayer interior, the hydrophobic tails (that is, the fatty acid portions of lipid molecules) interact by means of dispersion forces. The interactions are weakened by the presence of unsaturated fatty acids. As a result, the membrane components are free to mill about to some extent, and the membrane is described as fluid.

The lipids found in cell membranes can be categorized in various ways. Phospholipids are lipids containing phosphorus. Glycolipids are sugar-containing lipids. The latter are found exclusively on the outer surface of the cell membrane, acting as distinguishing surface markers for the cell and thus serving in cellular recognition and cell-to-cell communication. Sphingolipids

are phospholipids or glycolipids that contain the unsaturated amino alcohol sphingosine rather than glycerol. Diagrammatic structures of representative membrane lipids are presented in Figure **14.5.4**.

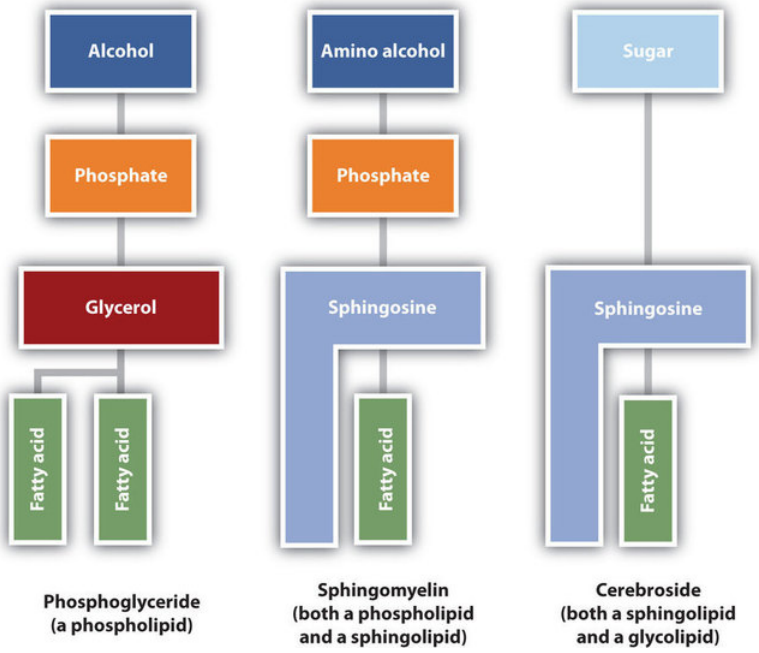



Figure **14.5.4**: Component Structures of Some Important Membrane Lipids

Phosphoglyceride are composed of alcohol, phosphate, glycerol and 2 fatty acids. A sphingomyelin contains phosphate, sphingosine, and a fatty acid. A cerbroside contains sugar, sphingosine and a fatty acid.

*Phosphoglycerides* (also known as glycerophospholipids) are the most abundant phospholipids in cell membranes. They consist of a glycerol unit with fatty acids attached to the first two carbon atoms, while a phosphoric acid unit, esterified with an alcohol molecule (usually an amino alcohol, as in part (a) of Figure **14.5.5**) is attached to the third carbon atom of glycerol (part (b) of Figure **14.5.5**). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure **14.5.5**).

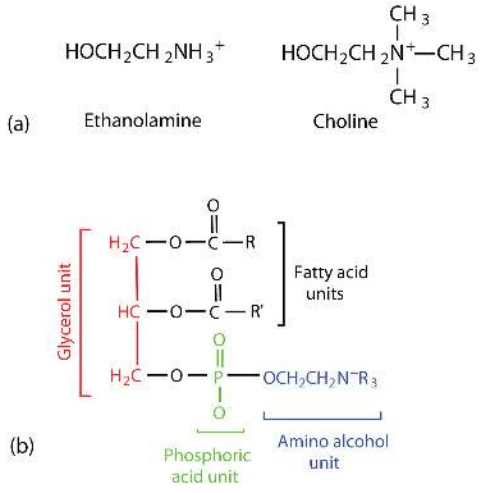
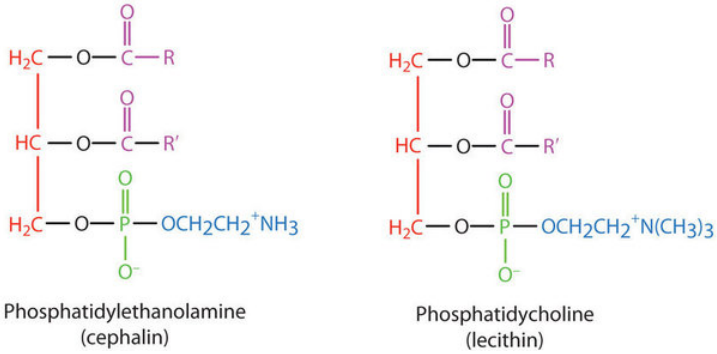



Figure **14.5.5**: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

Structural formula of ethanolamine and choline are shown. The structural formula of a phosphoglyceride is shown with the glycerol unit, phosphoric unit, and amino alcohol unit highlighted in different colors.

There are two common types of phosphoglycerides. Phosphoglycerides containing ethanolamine as the amino alcohol are called *phosphatidylethanolamines* or *cephalins*. Cephalins are found in brain tissue and nerves and also have a role in blood clotting. Phosphoglycerides containing choline as the amino alcohol unit are called *phosphatidylcholines* or *lecithins*. Lecithins occur in all

living organisms. Like cephalins, they are important constituents of nerve and brain tissue. Egg yolks are especially rich in lecithins. Commercial-grade lecithins isolated from soybeans are widely used in foods as emulsifying agents. An emulsifying agent is used to stabilize an emulsion—a dispersion of two liquids that do not normally mix, such as oil and water. Many foods are emulsions. Milk is an emulsion of butterfat in water. The emulsifying agent in milk is a protein called *casein*. Mayonnaise is an emulsion of salad oil in water, stabilized by lecithins present in egg yolk.




Sphingomyelins, the simplest sphingolipids, each contain a fatty acid, a phosphoric acid, sphingosine, and choline (Figure **14.5.6**). Because they contain phosphoric acid, they are also classified as phospholipids. Sphingomyelins are important constituents of the myelin sheath surrounding the axon of a nerve cell. Multiple sclerosis is one of several diseases resulting from damage to the myelin sheath.

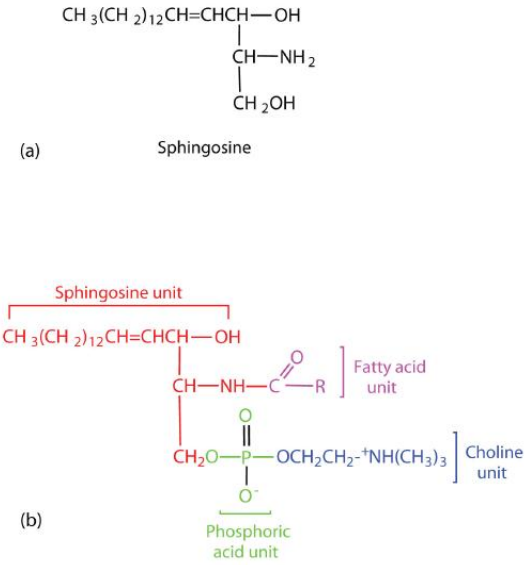



Figure **14.5.6**: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.

Structural formula of sphingosine is shown. The general structure of a sphingolipid is shown with the sphingosine unit, fatty acid unit, phosphoric acid unit, and choline unit highlighted in different colors.

Most animal cells contain sphingolipids called cerebrosides (Figure **14.5.7**). Cerebrosides are composed of sphingosine, a fatty acid, and galactose or glucose. They therefore resemble sphingomyelins but have a sugar unit in place of the choline phosphate group. Cerebrosides are important constituents of the membranes of nerve and brain cells.

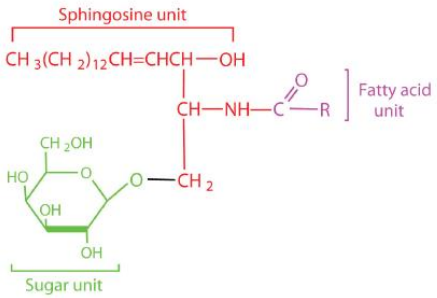



Figure 14.5.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.
General structure of a cerebroside with its sugar unit, sphingosine unit, and fatty acid unit highlighted in different colors.

The sphingolipids called gangliosides are more complex, usually containing a branched chain of three to eight monosaccharides and/or substituted sugars. Because of considerable variation in their sugar components, about 130 varieties of gangliosides have been identified. Most cell-to-cell recognition and communication processes (e.g., blood group antigens) depend on differences in the sequences of sugars in these compounds. Gangliosides are most prevalent in the outer membranes of nerve cells, although they also occur in smaller quantities in the outer membranes of most other cells. Because cerebrosides and gangliosides contain sugar groups, they are also classified as glycolipids.

## Membrane Proteins

If membranes were composed only of lipids, very few ions or polar molecules could pass through their hydrophobic "sandwich filling" to enter or leave any cell. However, certain charged and polar species do cross the membrane, aided by proteins that move about in the lipid bilayer. The two major classes of proteins in the cell membrane are integral proteins, which span the hydrophobic interior of the bilayer, and peripheral proteins, which are more loosely associated with the surface of the lipid bilayer (Figure **14.5.3**). Peripheral proteins may be attached to integral proteins, to the polar head groups of phospholipids, or to both by hydrogen bonding and electrostatic forces.

Small ions and molecules soluble in water enter and leave the cell by way of channels through the integral proteins. Some proteins, called *carrier proteins*, facilitate the passage of certain molecules, such as hormones and neurotransmitters, by specific interactions between the protein and the molecule being transported.

## Summary

Lipids are important components of biological membranes. These lipids have dual characteristics: part of the molecule is hydrophilic, and part of the molecule is hydrophobic. Membrane lipids may be classified as phospholipids, glycolipids, and/or sphingolipids. Proteins are another important component of biological membranes. Integral proteins span the lipid bilayer, while peripheral proteins are more loosely associated with the surface of the membrane.

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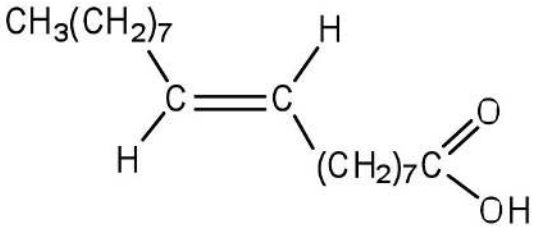
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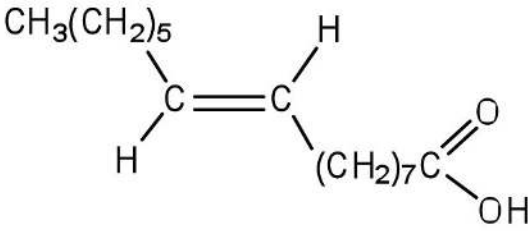
# 14.E: Exercises

## Additional Exercises

1. The melting point of elaidic acid is 52°C.
   a. What trend is observed when comparing the melting points of elaidic acid, oleic acid, and stearic acid? Explain.
   b. Would you expect the melting point of palmitelaidic acid to be lower or higher than that of elaidic acid? Explain.

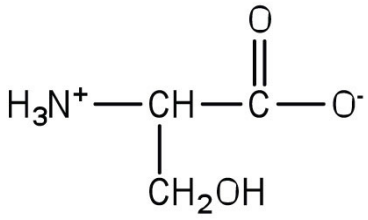


Elaidic acid



Palmitelaidic acid

2. Examine the labels on two brands of margarine and two brands of shortening and list the oils used in the various brands.
3. Draw a typical lecithin molecule that incorporates glycerol, palmitic acid, oleic acid, phosphoric acid, and choline. Circle all the ester bonds.
4. In cerebrosides, is the linkage between the fatty acid and sphingosine an amide bond or an ester bond? Justify your answer.
5. Serine is an amino acid that has the following structure. Draw the structure for a phosphatidylserine that contains a palmitic acid and a palmitoleic acid unit.

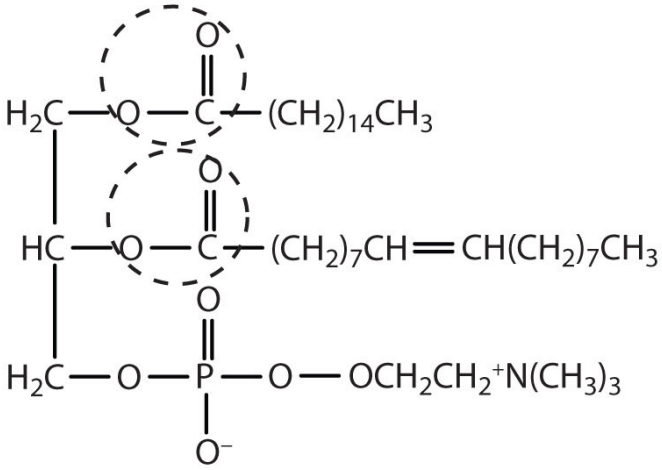


6. Explain whether each compound would be expected to diffuse through the lipid bilayer of a cell membrane.
   a. potassium chloride
   b. $CH_3CH_2CH_2CH_2CH_2CH_3$
   c. fructose
7. Identify the role of each steroid hormone in the body.
   a. progesterone
   b. aldosterone
   c. testosterone
   d. cortisol
8. How does the structure of cholic acid differ from that of cholesterol? Which compound would you expect to be more polar? Why?
9. a. What fatty acid is the precursor for the prostaglandins?
   b. Identify three biological effects of prostaglandins.
10. Why is it important to determine the ratio of LDLs to HDLs, rather than just the concentration of serum cholesterol?

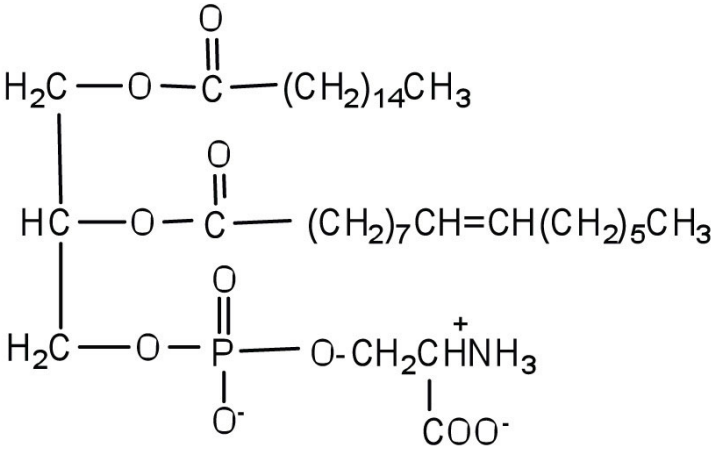
## Answers

1. a. Stearic acid has the highest melting point, followed by elaidic acid, and then oleic acid with the lowest melting point. Elaidic acid is a *trans* fatty acid, and the carbon chains can pack together almost as tightly as those of the saturated stearic acid. Oleic acid is a *cis* fatty acid, and the bend in the hydrocarbon chain keeps these carbon chains from packing as closely together; fewer interactions lead to a much lower melting point.
   b. The melting point of palmitelaidic acid should be lower than that of elaidic acid because it has a shorter carbon chain (16, as compared to 18 for elaidic acid). The shorter the carbon chain, the lower the melting point due to a decrease in intermolecular interactions.

3.



5.



7. a. regulates the menstrual cycle and maintains pregnancy
   b. regulates salt metabolism by stimulating the kidneys to retain sodium and excrete potassium
   c. stimulates and maintains male sex characteristics
   d. stimulates the conversion of proteins to carbohydrates

9. a. arachidonic acid
   b. induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response

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# 14.S: Lipids (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

**Lipids**, found in the body tissues of all organisms, are compounds that are more soluble in organic solvents than in water. Many of them contain **fatty acids**, which are carboxylic acids that generally contain an even number of 4–20 carbon atoms in an unbranched chain. **Saturated fatty acids** have no carbon-to-carbon double bonds. **Monounsaturated fatty acids** have a single carbon-to-carbon double bond, while **polyunsaturated fatty acids** have more than one carbon-to-carbon double bond. Linoleic and linolenic acid are known as **essential fatty acids** because the human body cannot synthesize these polyunsaturated fatty acids. The lipids known as **fats** and **oils** are triacylglycerols, more commonly called **triglycerides**—esters composed of three fatty acids joined to the trihydroxy alcohol glycerol. Fats are triglycerides that are solid at room temperature, and oils are triglycerides that are liquid at room temperature. Fats are found mainly in animals, and oils found mainly in plants. *Saturated triglycerides* are those containing a higher proportion of saturated fatty acid chains (fewer carbon-to-carbon double bonds); *unsaturated triglycerides* contain a higher proportion of unsaturated fatty acid chains.

**Saponification** is the hydrolysis of a triglyceride in a basic solution to form glycerol and three carboxylate anions or soap molecules. Other important reactions are the hydrogenation and oxidation of double bonds in unsaturated fats and oils.

**Phospholipids** are lipids containing phosphorus. In **phosphoglycerides**, the phosphorus is joined to an amino alcohol unit. Some phosphoglycerides, like lecithins, are used to stabilize an **emulsion**—a dispersion of two liquids that do not normally mix, such as oil and water. **Sphingolipids** are lipids for which the precursor is the amino alcohol sphingosine, rather than glycerol. A **glycolipid** has a sugar substituted at one of the OH groups of either glycerol or sphingosine. All are highly polar lipids found in cell membranes.

Polar lipids have dual characteristics: one part of the molecule is ionic and dissolves in water; the rest has a hydrocarbon structure and dissolves in nonpolar substances. Often, the ionic part is referred to as **hydrophilic** (literally, “water loving”) and the nonpolar part as **hydrophobic** (“water fearing”). When placed in water, polar lipids disperse into any one of three arrangements: *micelles*, *monolayers*, and *bilayers*. **Micelles** are aggregations of molecules in which the hydrocarbon tails of the lipids, being hydrophobic, are directed inward (away from the surrounding water), and the hydrophilic heads that are directed outward into the water. **Bilayers** are double layers arranged so that the hydrophobic tails are sandwiched between the two layers of hydrophilic heads, which remain in contact with the water.

Every living cell is enclosed by a *cell membrane* composed of a lipid bilayer. In animal cells, the bilayer consists mainly of phospholipids, glycolipids, and the steroid cholesterol. Embedded in the bilayer are **integral proteins**, and **peripheral proteins** are loosely associated with the surface of the bilayer. Everything between the cell membrane and the membrane of the cell nucleus is called the **cytoplasm**.

Most lipids can be saponified, but some, such as **steroids**, cannot be saponified. The steroid **cholesterol** is found in animal cells but never in plant cells. It is a main component of all cell membranes and a precursor for hormones, vitamin D, and bile salts. Bile salts are the most important constituents of **bile**, which is a yellowish-green liquid secreted by the gallbladder into the small intestine and is needed for the proper digestion of lipids.

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# CHAPTER OVERVIEW

## 15: Amino Acids, Proteins, and Enzymes

Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells. We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins. We end the chapter with a discussion of enzymes—the proteins that act as catalysts in the body.


15.1: Prelude to Amino Acids, Proteins, and Enzymes
15.2: Properties of Amino Acids
15.3: Reactions of Amino Acids
15.4: Peptides
15.5: Proteins
15.6: Enzymes
15.7: Enzyme Activity
15.8: Enzyme Action
15.9: Enzyme Inhibition
15.10: Enzyme Cofactors and Vitamins
15.E: Amino Acids, Proteins, and Enzymes (Exercises)
15.S: Amino Acids, Proteins, and Enzymes (Summary)


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# 15.1: Prelude to Amino Acids, Proteins, and Enzymes

The 1923 Nobel Prize in Medicine or Physiology was awarded to Frederick Grant Banting and John James Richard Macleod for their discovery of the protein *insulin*. In 1958, the Nobel Prize in Chemistry was awarded to Frederick Sanger for his discoveries concerning the structure of proteins and, in particular, the structure of insulin. What is so important about insulin that two Nobel Prizes have been awarded for work on this protein?

Insulin is a hormone that is synthesized in the pancreas. Insulin stimulates the transport of glucose into cells throughout the body and the storage of glucose as glycogen. People with diabetes do not produce insulin or use it properly. The isolation of insulin in 1921 led to the first effective treatment for these individuals.



Figure **15.1.1**: Insulin pump, showing an infusion set loaded into spring-loaded insertion device. A reservoir is attached to the infusion set (shown here removed from the pump). (Public Domain; User:David-i98 ).

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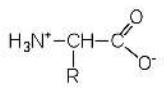
# 15.2: Properties of Amino Acids

**Learning Objectives**

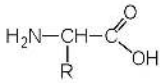
- To recognize amino acids and classify them based on the characteristics of their side chains.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.




α-Amino acid drawn as a zwitterion

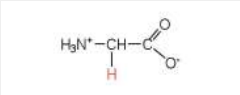
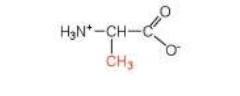
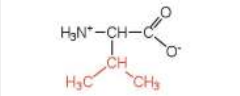
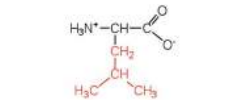
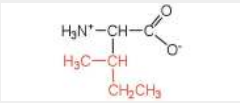
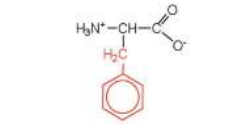
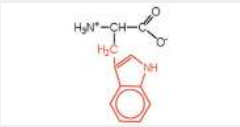
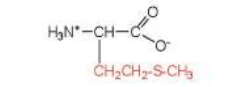
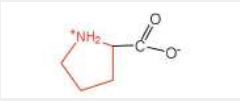
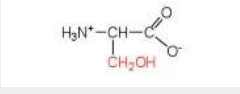
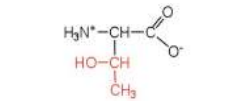
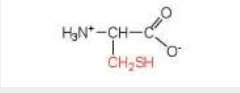


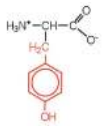
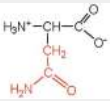
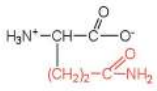
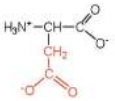
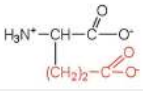
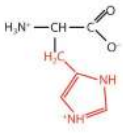
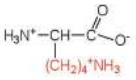
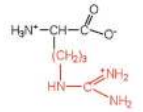

α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

## Classification

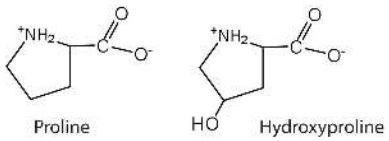
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the 20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table **15.2.1**.

Table **15.2.1**: Common Amino Acids Found in Proteins

| Common Name | Abbreviation | Structural Formula (at pH 6) | Molar Mass | Distinctive Feature |
|---|---|---|---|---|
| **Amino acids with a nonpolar R group** | | | | |
| glycine | gly (G) |  | 75 | the only amino acid lacking a chiral carbon |
| alanine | ala (A) |  | 89 | — |
| valine | val (V) |  | 117 | a branched-chain amino acid |
| leucine | leu (L) |  | 131 | a branched-chain amino acid |
| isoleucine | ile (I) |  | 131 | an essential amino acid because most animals cannot synthesize branched-chain amino acids |
| phenylalanine | phe (F) |  | 165 | also classified as an aromatic amino acid |
| tryptophan | trp (W) |  | 204 | also classified as an aromatic amino acid |
| methionine | met (M) |  | 149 | side chain functions as a methyl group donor |
| proline | pro (P) |  | 115 | contains a secondary amine group; referred to as an *α-imino acid* |
| **Amino acids with a polar but neutral R group** | | | | |
| serine | ser (S) |  | 105 | found at the active site of many enzymes |
| threonine | thr (T) |  | 119 | named for its similarity to the sugar threose |
| cysteine | cys (C) |  | 121 | oxidation of two cysteine molecules yields *cystine* |

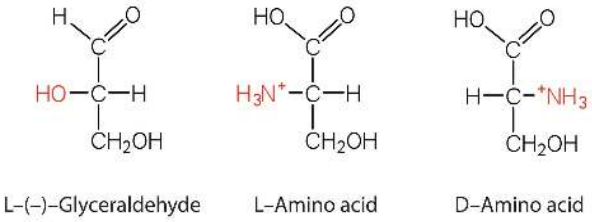
| Common Name | Abbreviation | Structural Formula (at pH 6) | Molar Mass | Distinctive Feature |
|---|---|---|---|---|
| tyrosine | tyr (Y) |  | 181 | also classified as an aromatic amino acid |
| asparagine | asn (N) |  | 132 | the amide of aspartic acid |
| glutamine | gln (Q) |  | 146 | the amide of glutamic acid |
| **Amino acids with a negatively charged R group** | | | | |
| aspartic acid | asp (D) |  | 132 | carboxyl groups are ionized at physiological pH; also known as aspartate |
| glutamic acid | glu (E) |  | 146 | carboxyl groups are ionized at physiological pH; also known as glutamate |
| **Amino acids with a positively charged R group** | | | | |
| histidine | his (H) |  | 155 | the only amino acid whose R group has a $pK_a$ (6.0) near physiological pH |
| lysine | lys (K) |  | 147 | — |
| arginine | arg (R) |  | 175 | almost as strong a base as sodium hydroxide |

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



## Configuration

Notice in Table **15.2.1** that glycine is the only amino acid whose α-carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as the reference compound for the assignment of absolute configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, an amino group takes the place of the OH group on the chiral carbon of the L-glyceraldehyde and a carboxylic acid replaces the aldehyde. Modern stereochemistry assignments using the Cahn-Ingold-Prelog priority rules used ubiquitously in chemistry show that all of the naturally occurring chiral amino acids are S except Cys which is R.




We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

## Summary

Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

## Concept Review Exercises

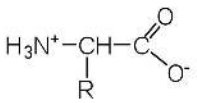
1. What is the general structure of an α-amino acid?
2. Identify the amino acid that fits each description.

a. also known as aspartate

b. almost as strong a base as sodium hydroxide

c. does not have a chiral carbon

Answer to #1:



Answer to #2:

a) aspartic acid

b) arginine

c) glycine

3. Write the side chain of each amino acid.

a. serine
b. arginine
c. phenylalanine

4. Draw the structure for each amino acid.

a. alanine

b. cysteine
c. histidine

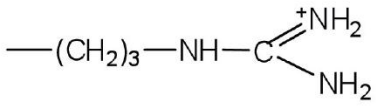
5. Identify an amino acid whose side chain contains a(n)

a. amide functional group.
b. aromatic ring.
c. carboxyl group.

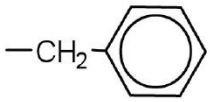
Answer to #3

a) $-CH_2-OH$

b)



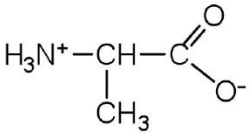
c)

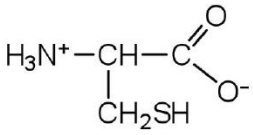


Answer to #4

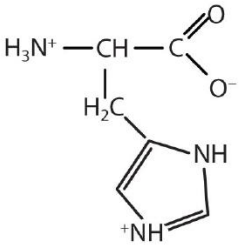
a)

b)





c)



Answer to # 5
a. asparagine or glutamine

b. phenylalanine, tyrosine, or tryptophan

c. aspartic acid or glutamic acid

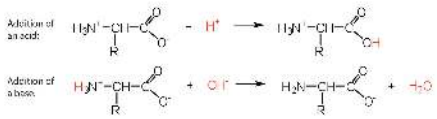
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## 15.3: Reactions of Amino Acids

**Learning Objectives**

- To explain how an amino acid can act as both an acid and a base.

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen ($H^+$) ion, and the amino acid becomes positively charged. If base is added, ion removal of the $H^+$ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid ($H^+$) or base ($OH^-$) from solution.

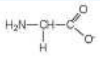



**Example 15.3.1**

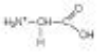
a. Draw the structure for the anion formed when glycine (at neutral pH) reacts with a base.
b. Draw the structure for the cation formed when glycine (at neutral pH) reacts with an acid.

**Solution**

a. The base removes $H^+$ from the protonated amine group.



b. The acid adds $H^+$ to the carboxylate group.



**Exercise 15.3.1**

a. Draw the structure for the cation formed when valine (at neutral pH) reacts with an acid.
b. Draw the structure for the anion formed when valine (at neutral pH) reacts with a base.

The particular pH at which a given amino acid exists in solution as a zwitterion is called the isoelectric point (pI). At its pI, the positive and negative charges on the amino acid balance, and the molecule as a whole is electrically neutral. The amino acids whose side chains are always neutral have isoelectric points ranging from 5.0 to 6.5. The basic amino acids (which have positively charged side chains at neutral pH) have relatively high examples. Acidic amino acids (which have negatively charged side chains at neutral pH) have quite low examples (Table **15.3.1**).

Table **15.3.1**: ExampIes of Some Representative Amino Acids

| Amino Acid | Classification |
|---|---|
| alanine | nonpolar |
| valine | nonpolar |
| serine | polar, uncharged |
| threonine | polar, uncharged |
| arginine | positively charged (basic) |
| histidine | positively charged (basic) |
| lysine | positively charged (basic) |
| aspartic acid | negatively charged (acidic) |
| glutamic acid | negatively charged (acidic) |

Amino acids undergo reactions characteristic of carboxylic acids and amines. The reactivity of these functional groups is particularly important in linking amino acids together to form peptides and proteins, as you will see later in this chapter. Simple chemical tests that are used to detect amino acids take advantage of the reactivity of these functional groups. An example is the ninhydrin test in which the amine functional group of α-amino acids reacts with ninhydrin to form purple-colored compounds. Ninhydrin is used to detect fingerprints because it reacts with amino acids from the proteins in skin cells transferred to the surface by the individual leaving the fingerprint.






### Summary

Amino acids can act as both an acid and a base due to the presence of the amino and carboxyl functional groups. The pH at which a given amino acid exists in solution as a zwitterion is called the *isoelectric point* (pI).

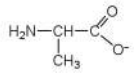
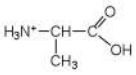
### Concept Review Exercises

1. Define each term.
   a. zwitterion

b. isoelectric point

2. Draw the structure for the anion formed when alanine (at neutral pH) reacts with a base.
3. Draw the structure for the cation formed when alanine (at neutral pH) reacts with an acid.

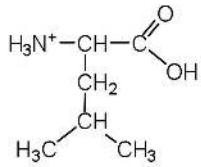
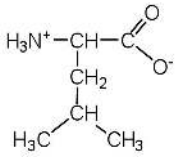
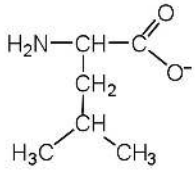
## Answers

1. a. an electrically neutral compound that contains both negatively and positively charged groups
   b. the pH at which a given amino acid exists in solution as a zwitterion
2. 
3. 

## Exercises

1. Draw the structure of leucine and determine the charge on the molecule in a(n)
   a. acidic solution (pH = 1).
   b. neutral solution (pH = 7).
   c. a basic solution (pH = 11)
2. Draw the structure of isoleucine and determine the charge on the molecule in a(n)
   a. acidic solution (pH = 1).
   b. neutral solution (pH = 7).
   c. basic solution (pH = 11).

## Answer

1. a. 
   b. 
   c. 

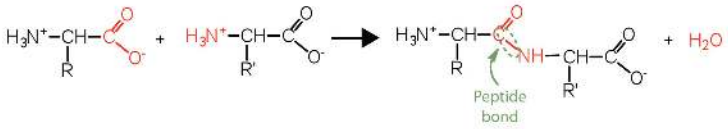
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# 15.4: Peptides

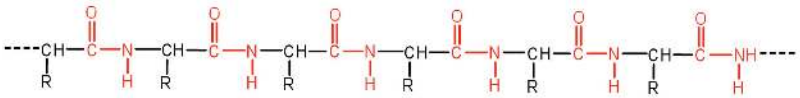
**Learning Objectives**

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

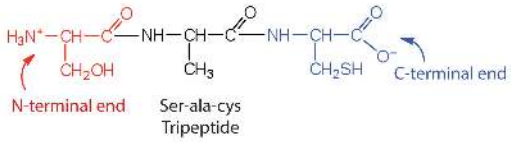
Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage:




An amide bond joining two amino acid units is called a peptide bond. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.



A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the N-terminal end) on the left and the amino acid with a free carboxyl group (the C-terminal end) to the right.




The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

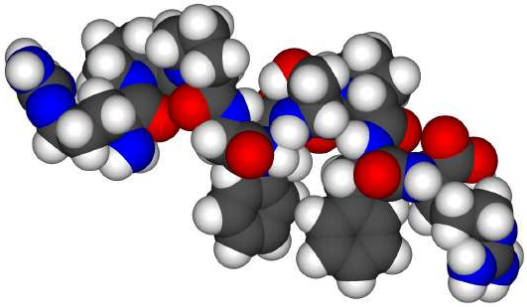


Figure **15.4.1**: Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order, or *sequence*, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure **15.4.1**) produced in the blood that has the following amino acid sequence:

**arg-pro-pro-gly-phe-ser-pro-phe-arg**

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

**arg-phe-pro-ser-phe-gly-pro-pro-arg**

the peptide resulting from this synthesis shows none of the activity of bradykinin.

Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of “incorrect” amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That “minor” error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

## Summary

The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together. Additional amino acids can be added on through the formation of addition peptide (amide) bonds. A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).

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# 15.5: Proteins

**Learning Objectives**

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain what happens when proteins are denatured.
- Identify how a protein can be denatured.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

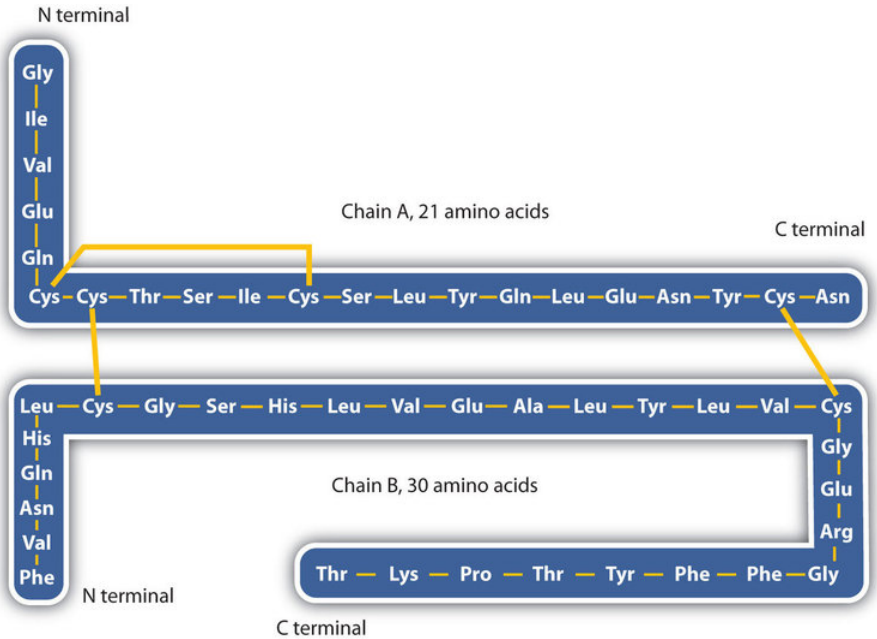



Figure 15.5.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

## Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the primary structure, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group

and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure **15.5.1**.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term secondary structure refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure **15.5.2**). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

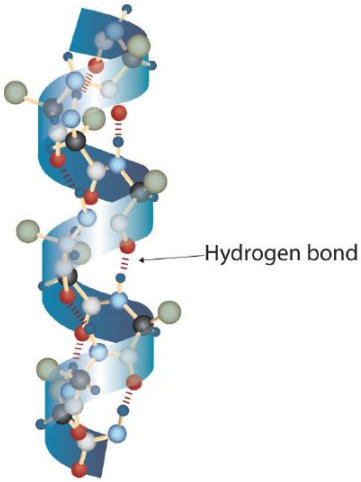



Figure **15.5.2** A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—and are connected by *interchain* hydrogen bonding (Figure **15.5.3**). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

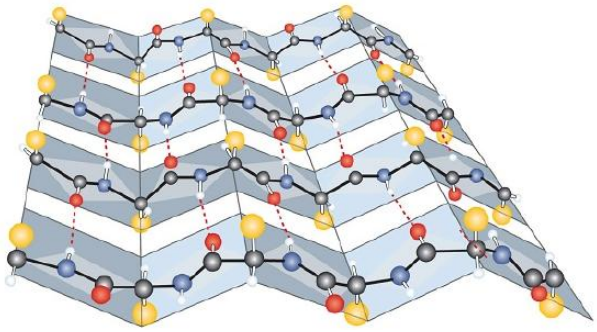


Figure **15.5.3**: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure **15.5.4** shows a depiction of the three-dimensional structure of insulin.

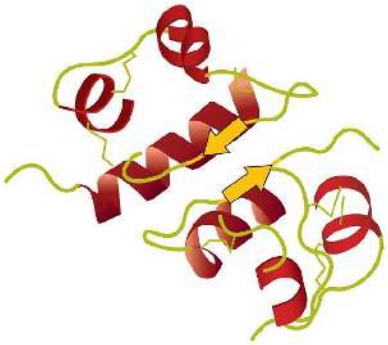
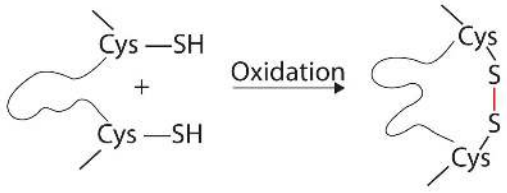


Figure 15.5.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins. You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure 15.5.5).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure 15.5.5).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure 15.5.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 15.5.1) and have a strong stabilizing effect on the tertiary structure.




4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure 15.5.5). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

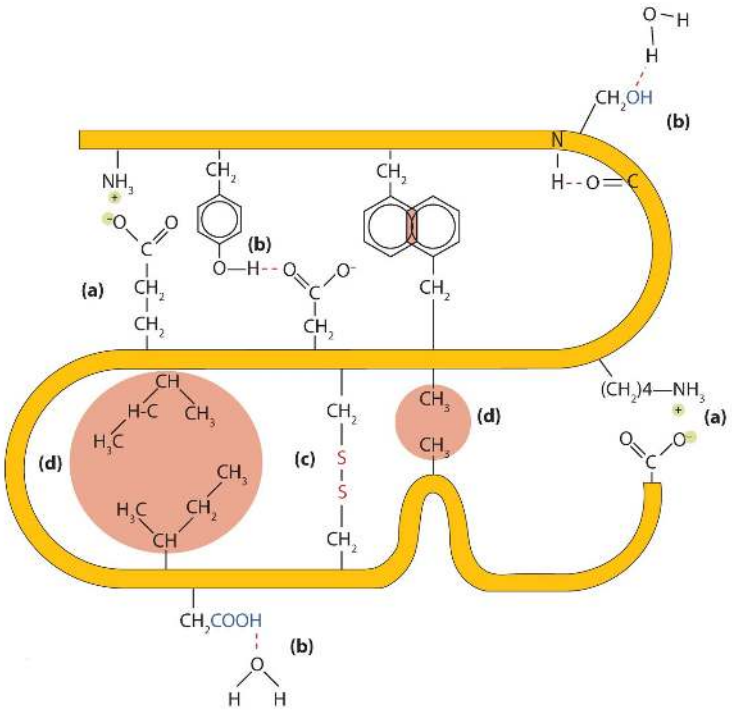



Figure 15.5.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 15.5.6). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 15.5.7.



Figure 15.5.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(opens in new window)) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

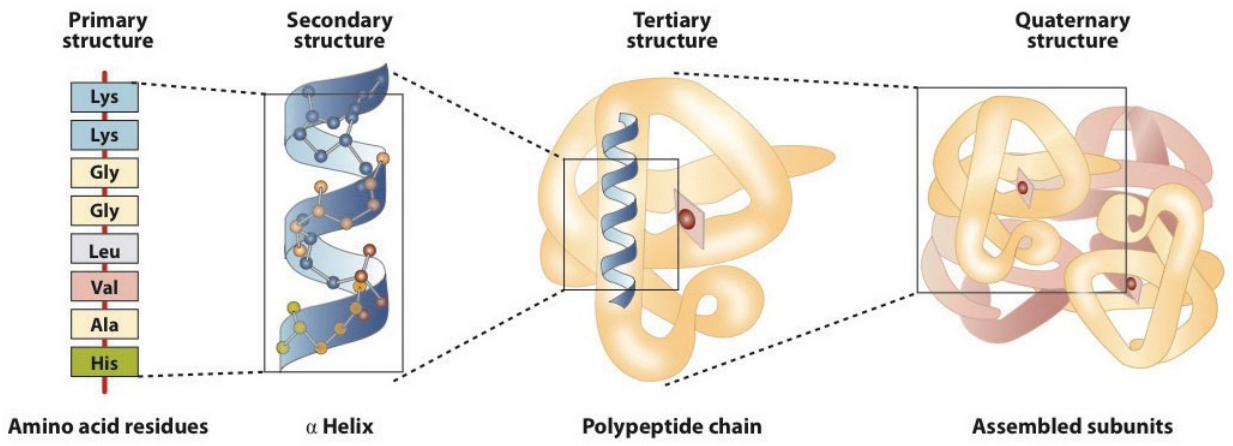



Figure **15.5.7**: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

## Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure **15.5.1**).

Figure **15.5.1**: Protein Denaturation Methods

| Method | Effect on Protein Structure |
|---|---|
| Heat above 50°C or ultraviolet (UV) radiation | Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces. |
| Use of organic compounds, such as ethyl alcohol | These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein. |
| Salts of heavy metal ions, such as mercury, silver, and lead | These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages. |
| Alkaloid reagents, such as tannic acid (used in tanning leather) | These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds. |

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure **15.5.8**). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

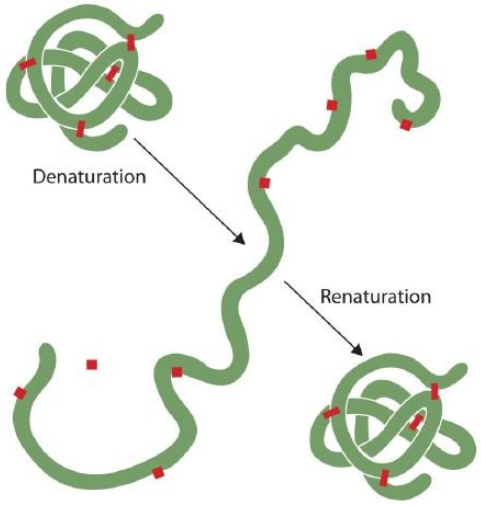



Figure **15.5.8**: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

## Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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# 15.6: Enzymes

**Learning Objectives**

- Explain the functions of enzymes.
- Explain how enzymes are classified and named.

A catalyst is any substance that increases the *rate* or speed of a chemical reaction without being changed or consumed in the reaction. Enzymes are biological catalysts, and nearly all of them are proteins. The reaction rates attained by enzymes are truly amazing. In their presence, reactions occur at rates that are a million ($10^6$) or more times faster than would be attainable in their absence. What is even more amazing is that enzymes perform this function at body temperature (~37°C) and physiological pH (pH ~7), rather than at the conditions that are typically necessary to increase reaction rates (high temperature or pressure, the use of strong oxidizing or reducing agents or strong acids or bases, or a combination of any of these). In addition, enzymes are highly specific in their action; that is, each enzyme catalyzes only one type of reaction in only one compound or a group of structurally related compounds. The compound or compounds on which an enzyme acts are known as its substrates.

Hundreds of enzymes have been purified and studied in an effort to understand how they work so effectively and with such specificity. The resulting knowledge has been used to design drugs that inhibit or activate particular enzymes. An example is the intensive research to improve the treatment of or find a cure for acquired immunodeficiency syndrome (AIDS). AIDS is caused by the human immunodeficiency virus (HIV). Researchers are studying the enzymes produced by this virus and are developing drugs intended to block the action of those enzymes without interfering with enzymes produced by the human body. Several of these drugs have now been approved for use by AIDS patients.

Table **15.6.1**: Classes of Enzymes

| Class | Type of Reaction Catalyzed | Examples |
|---|---|---|
| oxidoreductases | oxidation-reduction reactions | Dehydrogenases catalyze oxidation-reduction reactions involving hydrogen and reductases catalyze reactions in which a substrate is reduced. |
| transferases | transfer reactions of groups, such as methyl, amino, and acetyl | Transaminases catalyze the transfer of amino group, and kinases catalyze the transfer of a phosphate group. |
| hydrolases | hydrolysis reactions | Lipases catalyze the hydrolysis of lipids, and proteases catalyze the hydrolysis of proteins |
| lyases | reactions in which groups are removed without hydrolysis or addition of groups to a double bond | Decarboxylases catalyze the removal of carboxyl groups. |
| isomerases | reactions in which a compound is converted to its isomer | Isomerases may catalyze the conversion of an aldose to a ketose, and mutases catalyze reactions in which a functional group is transferred from one atom in a substrate to another. |
| ligases | reactions in which new bonds are formed between carbon and another atom; energy is required | Synthetases catalyze reactions in which two smaller molecules are linked to form a larger one. |

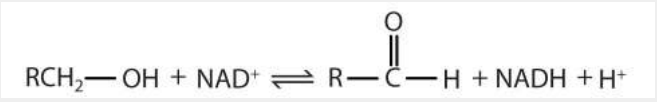
The first enzymes to be discovered were named according to their source or method of discovery. The enzyme *pepsin*, which aids in the hydrolysis of proteins, is found in the digestive juices of the stomach (Greek *pepsis*, meaning “digestion”). *Papain*, another

enzyme that hydrolyzes protein (in fact, it is used in meat tenderizers), is isolated from papayas. As more enzymes were discovered, chemists recognized the need for a more systematic and chemically informative identification scheme. In the current numbering and naming scheme, under the oversight of the Nomenclature Commission of the International Union of Biochemistry, enzymes are arranged into six groups according to the general type of reaction they catalyze (Table **15.6.1**), with subgroups and secondary subgroups that specify the reaction more precisely.

***Figure* 15.6.1*:*** *Structure of the alcohol dehydrogenase protein (E.C.1.1.1.1) (EE ISOZYME) complexed wtih nicotinamide adenini dinulceotide (NAD) and zinc (PDB: 1CDO).*

Each enzyme is assigned a four-digit number, preceded by the prefix EC—for enzyme classification—that indicates its group, subgroup, and so forth. This is demonstrated in Table **15.6.2** for alcohol dehydrogenase. Each enzyme is also given a name consisting of the root of the name of its substrate or substrates and the *-ase* suffix. Thus urease is the enzyme that catalyzes the hydrolysis of urea.

Table **15.6.2**: Assignment of an Enzyme Classification Number

| Alcohol Dehydrogenase: EC 1.1.1.1 | |
|---|---|
| The first digit indicates that this enzyme is an oxidoreductase; that is, an enzyme that catalyzes an oxidation-reduction reaction.<br>The second digit indicates that this oxidoreductase catalyzes a reaction involving a primary or secondary alcohol.<br>The third digit indicates that either the coenzyme $NAD^+$ or $NADP^+$ is required for this reaction. | |
| The fourth digit indicates that this was the first enzyme isolated, characterized, and named using this system of nomenclature. | |
| The systematic name for this enzyme is *alcohol:$NAD^+$ oxidoreductase*, while the recommended or common name is alcohol dehydrogenase. | |
| Reaction catalyzed: |  |

## Summary

An enzyme is a biological catalyst, a substance that increases the rate of a chemical reaction without being changed or consumed in the reaction. A systematic process is used to name and classify enzymes.

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# 15.7: Enzyme Activity

**Learning Objectives**

- To describe how pH, temperature, and the concentration of an enzyme and its substrate influence enzyme activity.

The single most important property of enzymes is the ability to increase the rates of reactions occurring in living organisms, a property known as *catalytic activity*. Because most enzymes are proteins, their activity is affected by factors that disrupt protein structure, as well as by factors that affect catalysts in general. Factors that disrupt protein structure include temperature and pH; factors that affect catalysts in general include reactant or substrate concentration and catalyst or enzyme concentration. The activity of an enzyme can be measured by monitoring either the rate at which a substrate disappears or the rate at which a product forms.

## Concentration of Substrate

In the presence of a given amount of enzyme, the rate of an enzymatic reaction increases as the substrate concentration increases until a limiting rate is reached, after which further increase in the substrate concentration produces no significant change in the reaction rate (part (a) of Figure 15.7.1). At this point, so much substrate is present that essentially all of the enzyme active sites have substrate bound to them. In other words, the enzyme molecules are saturated with substrate. The excess substrate molecules cannot react until the substrate already bound to the enzymes has reacted and been released (or been released without reacting).

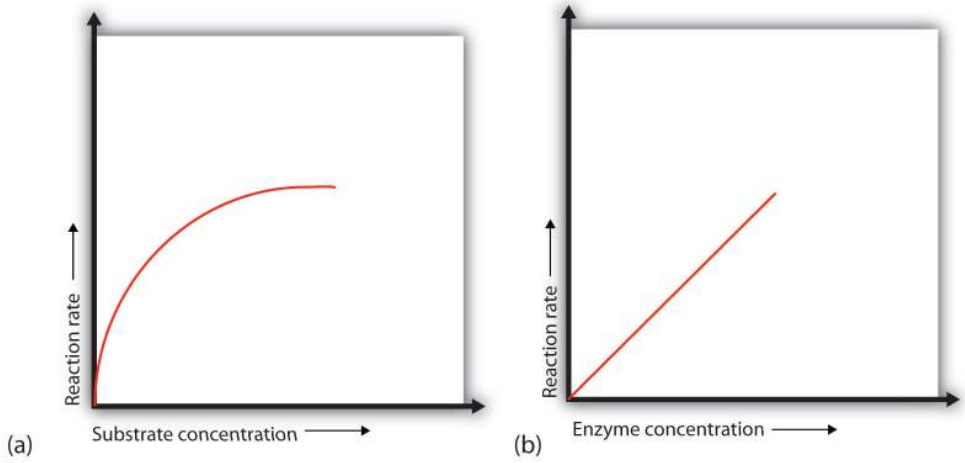



Figure 15.7.1: Concentration versus Reaction Rate. (a) This graph shows the effect of substrate concentration on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph shows the effect of enzyme concentration on the reaction rate at a constant level of substrate.

Let's consider an analogy. Ten taxis (enzyme molecules) are waiting at a taxi stand to take people (substrate) on a 10-minute trip to a concert hall, one passenger at a time. If only 5 people are present at the stand, the rate of their arrival at the concert hall is 5 people in 10 minutes. If the number of people at the stand is increased to 10, the rate increases to 10 arrivals in 10 minutes. With 20 people at the stand, the rate would still be 10 arrivals in 10 minutes. The taxis have been "saturated." If the taxis could carry 2 or 3 passengers each, the same principle would apply. The rate would simply be higher (20 or 30 people in 10 minutes) before it leveled off.

## Concentration of Enzyme

When the concentration of the enzyme is significantly lower than the concentration of the substrate (as when the number of taxis is far lower than the number of waiting passengers), the rate of an enzyme-catalyzed reaction is directly dependent on the enzyme concentration (part (b) of Figure 15.7.1). This is true for any catalyst; the reaction rate increases as the concentration of the catalyst is increased.

## Temperature

A general rule of thumb for most chemical reactions is that a temperature rise of 10°C approximately doubles the reaction rate. To some extent, this rule holds for all enzymatic reactions. After a certain point, however, an increase in temperature causes a decrease in the reaction rate, due to denaturation of the protein structure and disruption of the active site (part (a) of Figure **15.7.2**). For many proteins, denaturation occurs between 45°C and 55°C. Furthermore, even though an enzyme may appear to have a maximum reaction rate between 40°C and 50°C, most biochemical reactions are carried out at lower temperatures because enzymes are not stable at these higher temperatures and will denature after a few minutes.

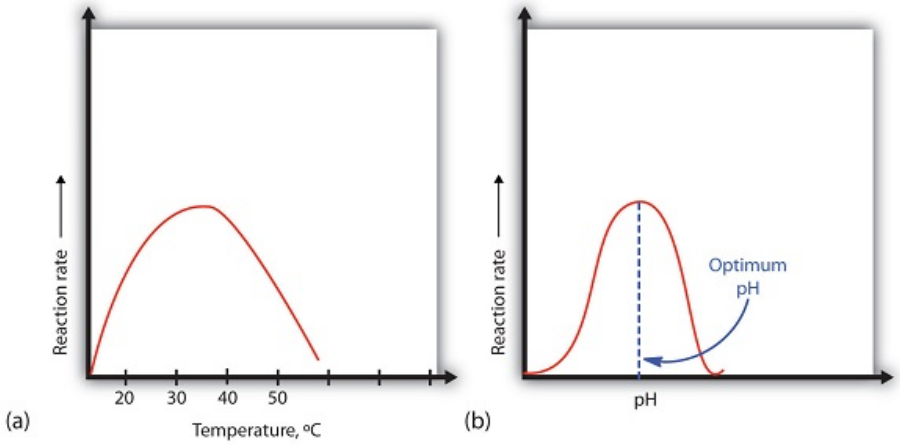



Figure **15.7.2**: Temperature and pH versus Concentration. (a) This graph depicts the effect of temperature on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph depicts the effect of pH on the rate of a reaction that is catalyzed by a fixed amount of enzyme.

At 0°C and 100°C, the rate of enzyme-catalyzed reactions is nearly zero. This fact has several practical applications. We sterilize objects by placing them in boiling water, which denatures the enzymes of any bacteria that may be in or on them. We preserve our food by refrigerating or freezing it, which slows enzyme activity. When animals go into hibernation in winter, their body temperature drops, decreasing the rates of their metabolic processes to levels that can be maintained by the amount of energy stored in the fat reserves in the animals' tissues.

## Hydrogen Ion Concentration (pH)

Because most enzymes are proteins, they are sensitive to changes in the hydrogen ion concentration or pH. Enzymes may be denatured by extreme levels of hydrogen ions (whether high or low); *any* change in pH, even a small one, alters the degree of ionization of an enzyme's acidic and basic side groups and the substrate components as well. Ionizable side groups located in the active site must have a certain charge for the enzyme to bind its substrate. Neutralization of even one of these charges alters an enzyme's catalytic activity.

An enzyme exhibits maximum activity over the narrow pH range in which a molecule exists in its properly charged form. The median value of this pH range is called the optimum pH of the enzyme (part (b) of Figure **15.7.2**). With the notable exception of gastric juice (the fluids secreted in the stomach), most body fluids have pH values between 6 and 8. Not surprisingly, most enzymes exhibit optimal activity in this pH range. However, a few enzymes have optimum pH values outside this range. For example, the optimum pH for pepsin, an enzyme that is active in the stomach, is 2.0.

## Summary

Initially, an increase in substrate concentration leads to an increase in the rate of an enzyme-catalyzed reaction. As the enzyme molecules become saturated with substrate, this increase in reaction rate levels off. The rate of an enzyme-catalyzed reaction increases with an increase in the concentration of an enzyme. At low temperatures, an increase in temperature increases the rate of an enzyme-catalyzed reaction. At higher temperatures, the protein is denatured, and the rate of the reaction dramatically decreases. An enzyme has an optimum pH range in which it exhibits maximum activity.

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# 15.8: Enzyme Action

**Learning Objectives**

- To describe the interaction between an enzyme and its substrate.

Enzyme-catalyzed reactions occur in at least two steps. In the first step, an enzyme molecule (E) and the substrate molecule or molecules (S) collide and react to form an intermediate compound called the *enzyme-substrate* (E–S) *complex*. (This step is reversible because the complex can break apart into the original substrate or substrates and the free enzyme.) Once the E–S complex forms, the enzyme is able to catalyze the formation of product (P), which is then released from the enzyme surface:

$$S + E \rightarrow E\text{–}S \tag{15.8.1}$$

$$E\text{–}S \rightarrow P + E \tag{15.8.2}$$

Hydrogen bonding and other electrostatic interactions hold the enzyme and substrate together in the complex. The structural features or functional groups on the enzyme that participate in these interactions are located in a cleft or pocket on the enzyme surface. This pocket, where the enzyme combines with the substrate and transforms the substrate to product is called the active site of the enzyme (Figure 15.8.1).

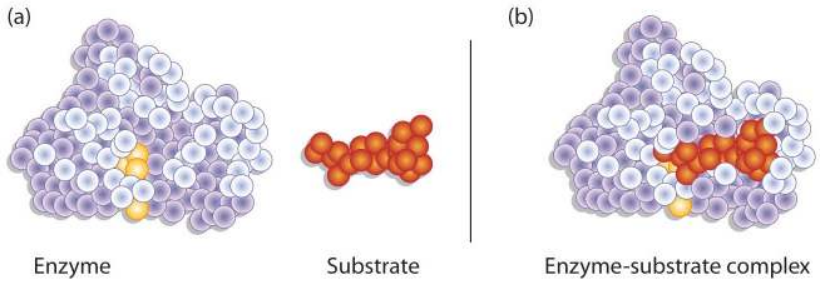



Figure 15.8.1: Substrate Binding to the Active Site of an Enzyme. The enzyme dihydrofolate reductase is shown with one of its substrates: $NADP^+$ (a) unbound and (b) bound. The $NADP^+$ (shown in red) binds to a pocket that is complementary to it in shape and ionic properties.

The active site of an enzyme possesses a unique conformation (including correctly positioned bonding groups) that is complementary to the structure of the substrate, so that the enzyme and substrate molecules fit together in much the same manner as a key fits into a tumbler lock. In fact, an early model describing the formation of the enzyme-substrate complex was called the lock-and-key model (Figure 15.8.2). This model portrayed the enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site.

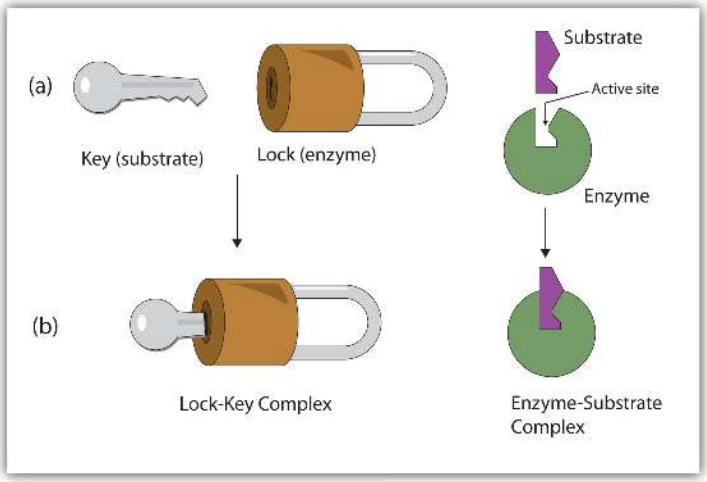



Figure 15.8.2: The Lock-and-Key Model of Enzyme Action. (a) Because the substrate and the active site of the enzyme have complementary structures and bonding groups, they fit together as a key fits a lock. (b) The catalytic reaction occurs while the two are bonded together in the enzyme-substrate complex.

Working out the precise three-dimensional structures of numerous enzymes has enabled chemists to refine the original lock-and-key model of enzyme actions. They discovered that the binding of a substrate often leads to a large conformational change in the enzyme, as well as to changes in the structure of the substrate or substrates. The current theory, known as the induced-fit model, says that enzymes can undergo a change in conformation when they bind substrate molecules, and the active site has a shape complementary to that of the substrate only *after* the substrate is bound, as shown for hexokinase in Figure 15.8.3. After catalysis, the enzyme resumes its original structure.

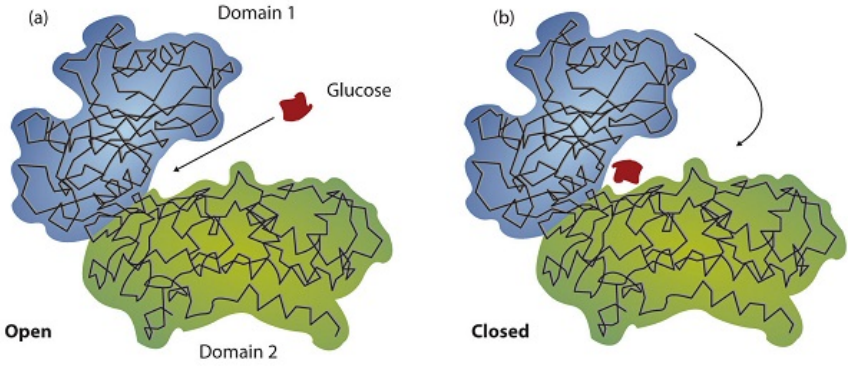



Figure 15.8.3: The Induced-Fit Model of Enzyme Action. (a) The enzyme hexokinase without its substrate (glucose, shown in red) is bound to the active site. (b) The enzyme conformation changes dramatically when the substrate binds to it, resulting in additional interactions between hexokinase and glucose.

The structural changes that occur when an enzyme and a substrate join together bring specific parts of a substrate into alignment with specific parts of the enzyme's active site. Amino acid side chains in or near the binding site can then act as acid or base catalysts, provide binding sites for the transfer of functional groups from one substrate to another or aid in the rearrangement of a substrate. The participating amino acids, which are usually widely separated in the primary sequence of the protein, are brought close together in the active site as a result of the folding and bending of the polypeptide chain or chains when the protein acquires its tertiary and quaternary structure. Binding to enzymes brings reactants close to each other and aligns them properly, which has the same effect as increasing the concentration of the reacting compounds.

### ✔ Example 15.8.1

a. What type of interaction would occur between an OH group present on a substrate molecule and a functional group in the active site of an enzyme?
b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

**Solution**

a. An OH group would most likely engage in hydrogen bonding with an appropriate functional group present in the active site of an enzyme.

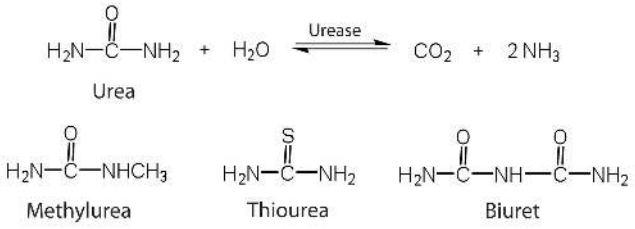
b. Several amino acid side chains would be able to engage in hydrogen bonding with an OH group. One example would be asparagine, which has an amide functional group.

**? Exercise 15.8.1**

a. What type of interaction would occur between an $COO^-$ group present on a substrate molecule and a functional group in the active site of an enzyme?

b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

One characteristic that distinguishes an enzyme from all other types of catalysts is its *substrate specificity*. An inorganic acid such as sulfuric acid can be used to increase the reaction rates of many different reactions, such as the hydrolysis of disaccharides, polysaccharides, lipids, and proteins, with complete impartiality. In contrast, enzymes are much more specific. Some enzymes act on a single substrate, while other enzymes act on any of a group of related molecules containing a similar functional group or chemical bond. Some enzymes even distinguish between D- and L-stereoisomers, binding one stereoisomer but not the other. Urease, for example, is an enzyme that catalyzes the hydrolysis of a single substrate—urea—but not the closely related compounds methyl urea, thiourea, or biuret. The enzyme carboxypeptidase, on the other hand, is far less specific. It catalyzes the removal of nearly any amino acid from the carboxyl end of any peptide or protein.




Enzyme specificity results from the uniqueness of the active site in each different enzyme because of the identity, charge, and spatial orientation of the functional groups located there. It regulates cell chemistry so that the proper reactions occur in the proper place at the proper time. Clearly, it is crucial to the proper functioning of the living cell.

## Summary

A substrate binds to a specific region on an enzyme known as the active site, where the substrate can be converted to product. The substrate binds to the enzyme primarily through hydrogen bonding and other electrostatic interactions. The induced-fit model says that an enzyme can undergo a conformational change when binding a substrate. Enzymes exhibit varying degrees of substrate specificity.

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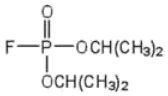
# 15.9: Enzyme Inhibition

**Learning Objectives**

- Explain what an enzyme inhibitor is.
- Distinguish between reversible and irreversible inhibitors.
- Distinguish between competitive and noncompetitive inhibitors.

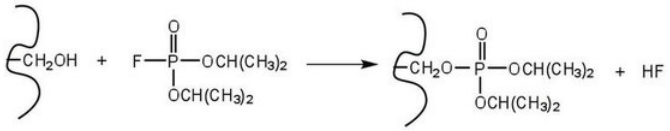
Previously, we noted that enzymes are inactivated at high temperatures and by changes in pH. These are nonspecific factors that would inactivate any enzyme. The activity of enzymes can also be regulated by more specific inhibitors. Many compounds are poisons because they bind covalently to particular enzymes or kinds of enzymes and inactivate them (Table **15.9.1**).

Table **15.9.1**: Poisons as Enzyme Inhibitors

| Poison | Formula | Example of Enzyme Inhibited | Action |
|---|---|---|---|
| arsenate | $AsO_4^{3-}$ | glyceraldehyde 3-phosphate dehydrogenase | substitutes for phosphate |
| iodoacetate | $ICH_2COO^-$ | triose phosphate dehydrogenase | binds to cysteine **SH** group |
| diisopropylfluoro-phosphate (DIFP; a nerve poison) |  | acetylcholinesterase | binds to serine **OH** group |

## Irreversible Inhibition: Poisons

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. The inhibitor-enzyme bond is so strong that the inhibition cannot be reversed by the addition of excess substrate. The nerve gases, especially Diisopropyl fluorophosphate (DIFP), irreversibly inhibit biological systems by forming an enzyme-inhibitor complex with a specific OH group of serine situated at the active sites of certain enzymes. The peptidases trypsin and chymotrypsin contain serine groups at the active site and are inhibited by DIFP.



## Reversible Inhibition

A reversible inhibitor inactivates an enzyme through noncovalent, more easily reversed, interactions. Unlike an irreversible inhibitor, a reversible inhibitor can dissociate from the enzyme. Reversible inhibitors include competitive inhibitors and noncompetitive inhibitors. (There are additional types of reversible inhibitors.) A competitive inhibitor is any compound that bears a structural resemblance to a particular substrate and thus competes with that substrate for binding at the active site of an enzyme. The inhibitor is not acted on by the enzyme but does prevent the substrate from approaching the active site.

The degree to which a competitive inhibitor interferes with an enzyme's activity depends on the relative concentrations of the substrate and the inhibitor. If the inhibitor is present in relatively large quantities, it will initially block most of the active sites. But because the binding is reversible, some substrate molecules will eventually bind to the active site and be converted to product. Increasing the substrate concentration promotes displacement of the inhibitor from the active site. Competitive inhibition can be completely reversed by adding substrate so that it reaches a much higher concentration than that of the inhibitor.

Studies of competitive inhibition have provided helpful information about certain enzyme-substrate complexes and the interactions of specific groups at the active sites. As a result, pharmaceutical companies have synthesized drugs that competitively inhibit metabolic processes in bacteria and certain cancer cells. Many drugs are competitive inhibitors of specific enzymes.

A classic example of competitive inhibition is the effect of malonate on the enzyme activity of succinate dehydrogenase (Figure 15.9.1). Malonate and succinate are the anions of dicarboxylic acids and contain three and four carbon atoms, respectively. The malonate molecule binds to the active site because the spacing of its carboxyl groups is not greatly different from that of succinate. However, no catalytic reaction occurs because malonate does not have a $CH_2CH_2$ group to convert to CH=CH. This reaction will also be discussed in connection with the Krebs cycle and energy production.

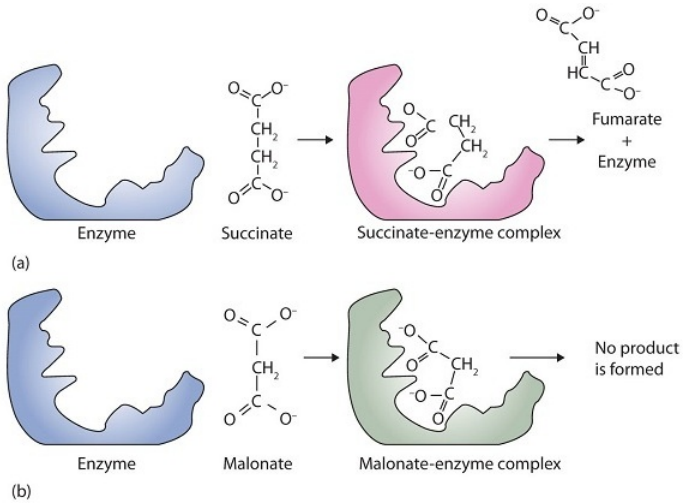



Figure 15.9.1: Competitive Inhibition. (a) Succinate binds to the enzyme succinate dehydrogenase. A dehydrogenation reaction occurs, and the product—fumarate—is released from the enzyme. (b) Malonate also binds to the active site of succinate dehydrogenase. In this case, however, no subsequent reaction occurs while malonate remains bound to the enzyme.

## To Your Health: Penicillin

*Chemotherapy* is the strategic use of chemicals (that is, drugs) to destroy infectious microorganisms or cancer cells without causing excessive damage to the other, healthy cells of the host. From bacteria to humans, the metabolic pathways of all living organisms are quite similar, so the search for safe and effective chemotherapeutic agents is a formidable task. Many well-established chemotherapeutic drugs function by inhibiting a critical enzyme in the cells of the invading organism.

An *antibiotic* is a compound that kills bacteria; it may come from a natural source such as molds or be synthesized with a structure analogous to a naturally occurring antibacterial compound. Antibiotics constitute no well-defined class of chemically related substances, but many of them work by effectively inhibiting a variety of enzymes essential to bacterial growth.

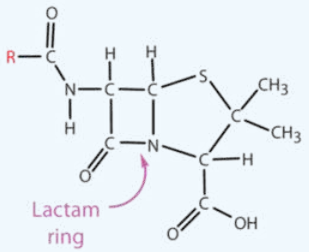
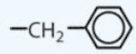
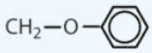
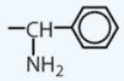
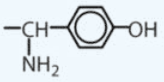
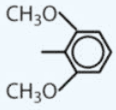
Penicillin, one of the most widely used antibiotics in the world, was fortuitously discovered by Alexander Fleming in 1928, when he noticed antibacterial properties in a mold growing on a bacterial culture plate. In 1938, Ernst Chain and Howard Florey began an intensive effort to isolate penicillin from the mold and study its properties. The large quantities of penicillin needed for this research became available through development of a corn-based nutrient medium that the mold loved and through the discovery of a higher-yielding strain of mold at a United States Department of Agriculture research center near Peoria, Illinois. Even so, it was not until 1944 that large quantities of penicillin were being produced and made available for the treatment of bacterial infections.

Penicillin functions by interfering with the synthesis of cell walls of reproducing bacteria. It does so by inhibiting an enzyme—transpeptidase—that catalyzes the last step in bacterial cell-wall biosynthesis. The defective walls cause bacterial cells to burst. Human cells are not affected because they have cell membranes, not cell walls.

Several naturally occurring penicillins have been isolated. They are distinguished by different R groups connected to a common structure: a four-member cyclic amide (called a lactam ring) fused to a five-member ring. The addition of appropriate organic compounds to the culture medium leads to the production of the different kinds of penicillin.

The penicillins are effective against gram-positive bacteria (bacteria capable of being stained by Gram's stain) and a few gram-negative bacteria (including the intestinal bacterium *Escherichia coli*). They are effective in the treatment of diphtheria, gonorrhea, pneumonia, syphilis, many pus infections, and certain types of boils. Penicillin G was the earliest penicillin to be used on a wide scale. However, it cannot be administered orally because it is quite unstable; the acidic pH of the stomach

converts it to an inactive derivative. The major oral penicillins—penicillin V, ampicillin, and amoxicillin—on the other hand, are acid stable.

| Penicillin Structure | R Group | Drug Name |
|---|---|---|
|  |  | penicillin G |
| |  | penicillin V |
| |  | ampicillin |
| |  | amoxicillin |
| |  | methicillin |

Some strains of bacteria become resistant to penicillin through a mutation that allows them to synthesize an enzyme—penicillinase—that breaks the antibiotic down (by cleavage of the amide linkage in the lactam ring). To combat these strains, scientists have synthesized penicillin analogs (such as methicillin) that are not inactivated by penicillinase.

Some people (perhaps 5% of the population) are allergic to penicillin and therefore must be treated with other antibiotics. Their allergic reaction can be so severe that a fatal coma may occur if penicillin is inadvertently administered to them. Fortunately, several other antibiotics have been discovered. Most, including aureomycin and streptomycin, are the products of microbial synthesis. Others, such as the semisynthetic penicillins and tetracyclines, are made by chemical modifications of antibiotics; and some, like chloramphenicol, are manufactured entirely by chemical synthesis. They are as effective as penicillin in destroying infectious microorganisms. Many of these antibiotics exert their effects by blocking protein synthesis in microorganisms.

Initially, antibiotics were considered miracle drugs, substantially reducing the number of deaths from blood poisoning, pneumonia, and other infectious diseases. Some seven decades ago, a person with a major infection almost always died. Today, such deaths are rare. Seven decades ago, pneumonia was a dreaded killer of people of all ages. Today, it kills only the very old or those ill from other causes. Antibiotics have indeed worked miracles in our time, but even miracle drugs have limitations. Not long after the drugs were first used, disease organisms began to develop strains resistant to them. In a race to stay ahead of resistant bacterial strains, scientists continue to seek new antibiotics. The penicillins have now been partially displaced by related compounds, such as the cephalosporins and vancomycin. Unfortunately, some strains of bacteria have already shown resistance to these antibiotics.

Some reversible inhibitors are noncompetitive. A noncompetitive inhibitor can combine with either the free enzyme or the enzyme-substrate complex because its binding site on the enzyme is distinct from the active site. Binding of this kind of inhibitor alters the three-dimensional conformation of the enzyme, changing the configuration of the active site with one of two results. Either the enzyme-substrate complex does not form at its normal rate, or, once formed, it does not yield products at the normal rate. Because the inhibitor does not structurally resemble the substrate, the addition of excess substrate does *not* reverse the inhibitory effect.

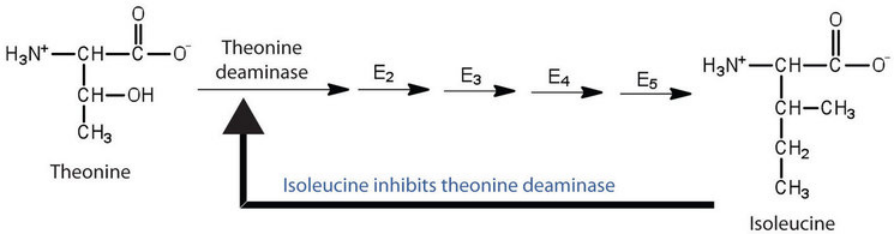



Figure **15.9.2**: Feedback Inhibition of Threonine Deaminase by Isoleucine. Threonine deaminase is the first enzyme in the conversion of threonine to isoleucine. Isoleucine inhibits threonine deaminase through feedback inhibition.

Feedback inhibition is a normal biochemical process that makes use of noncompetitive inhibitors to control some enzymatic activity. In this process, the final product inhibits the enzyme that catalyzes the first step in a series of reactions. Feedback inhibition is used to regulate the synthesis of many amino acids. For example, bacteria synthesize isoleucine from threonine in a series of five enzyme-catalyzed steps. As the concentration of isoleucine increases, some of it binds as a noncompetitive inhibitor to the first enzyme of the series (threonine deaminase), thus bringing about a decrease in the amount of isoleucine being formed (Figure **15.9.2**).

## Summary

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. A reversible inhibitor inactivates an enzyme through noncovalent, reversible interactions. A competitive inhibitor competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site.

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https://chem.libretexts.org/@go/page/288378

# 15.10: Enzyme Cofactors and Vitamins

**Learning Objectives**

- To explain why vitamins are necessary in the diet.

Many enzymes are simple proteins consisting entirely of one or more amino acid chains. Other enzymes contain a nonprotein component called a **cofactor** that is necessary for the enzyme's proper functioning. There are two types of cofactors: inorganic ions [e.g., zinc or Cu(I) ions] and organic molecules known as coenzymes. Most **coenzymes** are vitamins or are derived from vitamins.

Vitamins are organic compounds that are essential in very small (trace) amounts for the maintenance of normal metabolism. They generally cannot be synthesized at adequate levels by the body and must be obtained from the diet. The absence or shortage of a vitamin may result in a vitamin-deficiency disease. In the first half of the 20th century, a major focus of biochemistry was the identification, isolation, and characterization of vitamins. Despite accumulating evidence that people needed more than just carbohydrates, fats, and proteins in their diets for normal growth and health, it was not until the early 1900s that research established the need for trace nutrients in the diet.

Table **15.10.1**: Fat-Soluble Vitamins and Physiological Functions

| Vitamin | Physiological Function | Effect of Deficiency |
|---|---|---|
| vitamin A (retinol) | formation of vision pigments; differentiation of epithelial cells | night blindness; continued deficiency leads to total blindness |
| vitamin D (cholecalciferol) | increases the body's ability to absorb calcium and phosphorus | osteomalacia (softening of the bones); known as rickets in children |
| vitamin E (tocopherol) | fat-soluble antioxidant | damage to cell membranes |
| vitamin K (phylloquinone) | formation of prothrombin, a key enzyme in the blood-clotting process | increases the time required for blood to clot |

Because organisms differ in their synthetic abilities, a substance that is a vitamin for one species may not be so for another. Over the past 100 years, scientists have identified and isolated 13 vitamins required in the human diet and have divided them into two broad categories: the *fat-soluble vitamins*, which include vitamins A, D, E, and K, and the *water-soluble vitamins*, which are the B complex vitamins and vitamin C. All fat-soluble vitamins contain a high proportion of hydrocarbon structural components. There are one or two oxygen atoms present, but the compounds as a whole are nonpolar. In contrast, water-soluble vitamins contain large numbers of electronegative oxygen and nitrogen atoms, which can engage in hydrogen bonding with water. Most water-soluble vitamins act as coenzymes or are required for the synthesis of coenzymes. The fat-soluble vitamins are important for a variety of physiological functions. The key vitamins and their functions are found in Tables **15.10.1** and **15.10.2**.

Table **15.10.2**: Water-Soluble Vitamins and Physiological Functions

| Vitamin | Coenzyme | Coenzyme Function | Deficiency Disease |
|---|---|---|---|
| vitamin $B_1$ (thiamine) | thiamine pyrophosphate | decarboxylation reactions | beri-beri |
| vitamin $B_2$ (riboflavin) | flavin mononucleotide or flavin adenine dinucleotide | oxidation-reduction reactions involving two hydrogen atoms | — |
| vitamin $B_3$ (niacin) | nicotinamide adenine dinucleotide or nicotinamide adenine dinucleotide phosphate | oxidation-reduction reactions involving the hydride ion ($H^-$) | pellagra |
| vitamin $B_6$ (pyridoxine) | pyridoxal phosphate | variety of reactions including the transfer of amino groups | — |
| vitamin $B_{12}$ (cyanocobalamin) | methylcobalamin or deoxyadenoxylcobalamin | intramolecular rearrangement reactions | pernicious anemia |
| biotin | biotin | carboxylation reactions | — |
| folic acid | tetrahydrofolate | carrier of one-carbon units such as the formyl group | anemia |
| pantothenic Acid | coenzyme A | carrier of acyl groups | — |
| vitamin C (ascorbic acid) | none | antioxidant; formation of collagen, a protein found in tendons, ligaments, and bone | scurvy |

Vitamins C and E, as well as the provitamin β-carotene can act as antioxidants in the body. Antioxidants prevent damage from free radicals, which are molecules that are highly reactive because they have unpaired electrons. Free radicals are formed not only through metabolic reactions involving oxygen but also by such environmental factors as radiation and pollution.

> *β-carotene is known as a provitamin because it can be converted to vitamin A in the body.*

Free radicals react most commonly react with lipoproteins and unsaturated fatty acids in cell membranes, removing an electron from those molecules and thus generating a new free radical. The process becomes a chain reaction that finally leads to the oxidative degradation of the affected compounds. Antioxidants react with free radicals to stop these chain reactions by forming a more stable molecule or, in the case of vitamin E, a free radical that is much less reactive (vitamin E is converted back to its original form through interaction with vitamin C).

## Summary

Vitamins are organic compounds that are essential in very small amounts for the maintenance of normal metabolism. Vitamins are divided into two broad categories: fat-soluble vitamins and water-soluble vitamins. Most water-soluble vitamins are needed for the formation of coenzymes, which are organic molecules needed by some enzymes for catalytic activity.

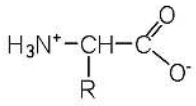
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# 15.E: Amino Acids, Proteins, and Enzymes (Exercises)

## 18.1: Properties of Amino Acids

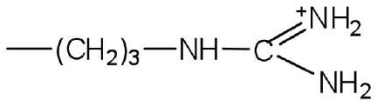
### Concept Review Exercises

1. What is the general structure of an α-amino acid?
2. Identify the amino acid that fits each description.
   a. also known as aspartate
   b. almost as strong a base as sodium hydroxide
   c. does not have a chiral carbon
3. 

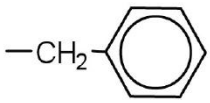
4. a. aspartic acid
   b. arginine
   c. glycine
5. Write the side chain of each amino acid.
   a. serine
   b. arginine
   c. phenylalanine
6. Write the side chain of each amino acid.
   a. aspartic acid
   b. methionine
   c. valine
7. Draw the structure for each amino acid.
   a. alanine
   b. cysteine
   c. histidine
8. Draw the structure for each amino acid.
   a. threonine
   b. glutamic acid
   c. leucine
9. Identify an amino acid whose side chain contains a(n)
   a. amide functional group.
   b. aromatic ring.
   c. carboxyl group.
10. Identify an amino acid whose side chain contains a(n)
    a. OH group
    b. branched chain
    c. amino group

1. a. $CH_2OH^-$

b.

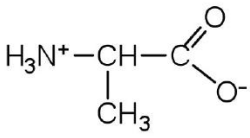


c.

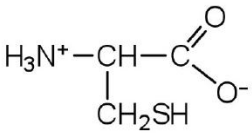


2.

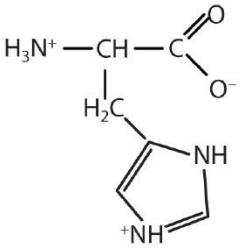
3. a.



b.



c.



4.

5. a. asparagine or glutamine
   b. phenylalanine, tyrosine, or tryptophan
   c. aspartic acid or glutamic acid

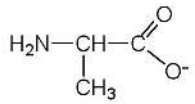
## 18.2: Reactions of Amino Acids

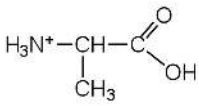
### Concept Review Exercises

1. Define each term.
   a. zwitterion
   b. isoelectric point
2. Draw the structure for the anion formed when alanine (at neutral pH) reacts with a base.
3. Draw the structure for the cation formed when alanine (at neutral pH) reacts with an acid.

### Answers

1. a. an electrically neutral compound that contains both negatively and positively charged groups
   b. the pH at which a given amino acid exists in solution as a zwitterion

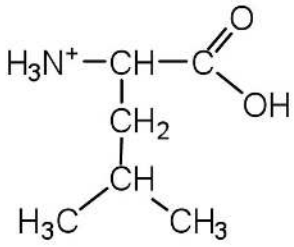
2. 

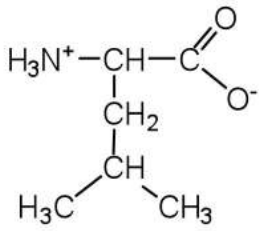
3. 

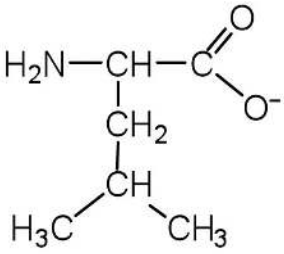
## Exercises

1. Draw the structure of leucine and determine the charge on the molecule in a(n)
   a. acidic solution (pH = 1).
   b. neutral solution (pH = 7).
   c. a basic solution (pH = 11)
2. Draw the structure of isoleucine and determine the charge on the molecule in a(n)
   a. acidic solution (pH = 1).
   b. neutral solution (pH = 7).
   c. basic solution (pH = 11).

## Answer

1. a. 

   b. 

   c. 

## 18.3: Peptides

## Concept Review Exercises

1. Distinguish between the N-terminal amino acid and the C-terminal amino acid of a peptide or protein.
2. Describe the difference between an amino acid and a peptide.
3. Amino acid units in a protein are connected by peptide bonds. What is another name for the functional group linking the amino acids?

## Answers

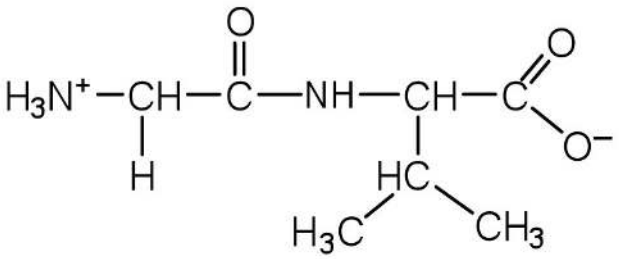
1. The N-terminal end is the end of a peptide or protein whose amino group is free (not involved in the formation of a peptide bond), while the C-terminal end has a free carboxyl group.
2. A peptide is composed of two or more amino acids. Amino acids are the building blocks of peptides.
3. amide bond

## Exercises

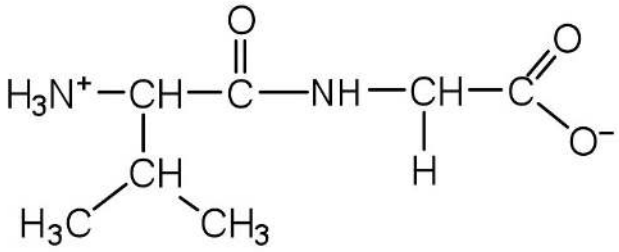
1. Draw the structure for each peptide.
   a. gly-val
   b. val-gly
2. Draw the structure for cys-val-ala.
3. Identify the C- and N-terminal amino acids for the peptide lys-val-phe-gly-arg-cys.
4. Identify the C- and N-terminal amino acids for the peptide asp-arg-val-tyr-ile-his-pro-phe.

## Answers

1. a.



   b.



3. C-terminal amino acid: cys; N-terminal amino acid: lys

# 18.4: Proteins

## Concept Review Exercises

1. What is the predominant attractive force that stabilizes the formation of secondary structure in proteins?
2. Distinguish between the tertiary and quaternary levels of protein structure.
3. Briefly describe four ways in which a protein could be denatured.

## Answers

1. hydrogen bonding
2. Tertiary structure refers to the unique three-dimensional shape of a single polypeptide chain, while quaternary structure describes the interaction between multiple polypeptide chains for proteins that have more than one polypeptide chain.
3. (1) heat a protein above 50°C or expose it to UV radiation; (2) add organic solvents, such as ethyl alcohol, to a protein solution; (3) add salts of heavy metal ions, such as mercury, silver, or lead; and (4) add alkaloid reagents such as tannic acid

## Exercises

1. Classify each protein as fibrous or globular.
   a. albumin
   b. myosin
   c. fibroin
2. Classify each protein as fibrous or globular.
   a. hemoglobin
   b. keratin
   c. myoglobin
3. What name is given to the predominant secondary structure found in silk?
4. What name is given to the predominant secondary structure found in wool protein?
5. A protein has a tertiary structure formed by interactions between the side chains of the following pairs of amino acids. For each pair, identify the strongest type of interaction between these amino acids.
   a. aspartic acid and lysine
   b. phenylalanine and alanine
   c. serine and lysine
   d. two cysteines
6. A protein has a tertiary structure formed by interactions between the side chains of the following pairs of amino acids. For each pair, identify the strongest type of interaction between these amino acids.
   a. valine and isoleucine
   b. asparagine and serine
   c. glutamic acid and arginine
   d. tryptophan and methionine
7. What level(s) of protein structure is(are) ordinarily disrupted in denaturation? What level(s) is(are) not?
8. Which class of proteins is more easily denatured—fibrous or globular?

## Answers

1. a. globular
   b. fibrous
   c. fibrous
3. β-pleated sheet
5. a. ionic bonding
   b. dispersion forces
   c. dispersion forces
   d. disulfide linkage
7. Protein denaturation disrupts the secondary, tertiary, and quaternary levels of structure. Only primary structure is unaffected by denaturation.

## 18.5: Enzymes

### Concept Review Exercise

In the small intestine, sucrose is hydrolyzed to form glucose and fructose in a reaction catalyzed by sucrase.

1. Identify the substrate in this reaction.
2. Name the enzyme.

### Answers

1. sucrose
2. sucrase

### Exercises

1. Identify the substrate catalyzed by each enzyme.
    a. lactase
    b. cellulase
    c. peptidase
2. Identify the substrate catalyzed by each enzyme.
    a. lipase
    b. amylase
    c. maltase
3. Identify each type of enzyme.
    a. decarboxylase
    b. protease
    c. transaminase
4. Identify each type of enzyme.
    a. dehydrogenase
    b. isomerase
    c. lipase

### Answers

1. a. lactose
    b. cellulose
    c. peptides
3. a. lyase
    b. hydrolase
    c. transferase

## 18.6: Enzyme Action

### Concept Review Exercises

1. Distinguish between the lock-and-key model and induced-fit model of enzyme action.
2. Which enzyme has greater specificity—urease or carboxypeptidase? Explain.

## Answers

1. The lock-and-key model portrays an enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site. The induced fit model portrays the enzyme structure as more flexible and is complementary to the substrate only after the substrate is bound.
2. Urease has the greater specificity because it can bind only to a single substrate. Carboxypeptidase, on the other hand, can catalyze the removal of nearly any amino acid from the carboxyl end of a peptide or protein.

## Exercises

1. What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?
   a. COOH
   b. $NH_3^+$
   c. OH
   d. $CH(CH_3)_2$
2. What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?
   a. SH
   b. $NH_2$
   c. $C_6H_5$
   d. $COO^-$
3. For each functional group in Exercise 1, suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you identified.
4. For each functional group in Exercise 2, suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you identified.

## Answers

1. a. hydrogen bonding
   b. ionic bonding
   c. hydrogen bonding
   d. dispersion forces
3. a. The amino acid has a polar side chain capable of engaging in hydrogen bonding; serine (answers will vary).
   b. The amino acid has a negatively charged side chain; aspartic acid (answers will vary).
   c. The amino acid has a polar side chain capable of engaging in hydrogen bonding; asparagine (answers will vary).
   d. The amino acid has a nonpolar side chain; isoleucine (answers will vary).

# 18.7: Enzyme Activity

## Concept Review Exercises

1. The concentration of substrate X is low. What happens to the rate of the enzyme-catalyzed reaction if the concentration of X is doubled?
2. What effect does an increase in the enzyme concentration have on the rate of an enzyme-catalyzed reaction?

## Answers

1. If the concentration of the substrate is low, increasing its concentration will increase the rate of the reaction.
2. An increase in the amount of enzyme will increase the rate of the reaction (provided sufficient substrate is present).

## Exercises

1. In non-enzyme-catalyzed reactions, the reaction rate increases as the concentration of reactant is increased. In an enzyme-catalyzed reaction, the reaction rate initially increases as the substrate concentration is increased but then begins to level off, so that the increase in reaction rate becomes less and less as the substrate concentration increases. Explain this difference.
2. Why do enzymes become inactive at very high temperatures?
3. An enzyme has an optimum pH of 7.4. What is most likely to happen to the activity of the enzyme if the pH drops to 6.3? Explain.
4. An enzyme has an optimum pH of 7.2. What is most likely to happen to the activity of the enzyme if the pH increases to 8.5? Explain.

## Answers

1. In an enzyme-catalyzed reaction, the substrate binds to the enzyme to form an enzyme-substrate complex. If more substrate is present than enzyme, all of the enzyme binding sites will have substrate bound, and further increases in substrate concentration cannot increase the rate.
3. The activity will decrease; a pH of 6.3 is more acidic than 7.4, and one or more key groups in the active site may bind a hydrogen ion, changing the charge on that group.

# 18.8: Enzyme Inhibition

## Concept Review Exercises

1. What is the difference between a cofactor and a coenzyme?
2. How are vitamins related to coenzymes?

## Answers

1. A coenzyme is one type of cofactor. Coenzymes are organic molecules required by some enzymes for activity. A cofactor can be either a coenzyme or an inorganic ion.
2. Coenzymes are synthesized from vitamins.

## Exercises

1. Identify each vitamin as water soluble or fat soluble.
    a. vitamin D
    b. vitamin C
    c. vitamin $B_{12}$
2. Identify each vitamin as water soluble or fat soluble.
    a. niacin
    b. cholecalciferol
    c. biotin
3. What vitamin is needed to form each coenzyme?
    a. pyridoxal phosphate
    b. flavin adenine dinucleotide
    c. coenzyme A
    d. nicotinamide adenine dinucleotide
4. What coenzyme is formed from each vitamin?
    a. niacin
    b. thiamine
    c. cyanocobalamin
    d. pantothenic acid

5. What is the function of each vitamin or coenzyme?
   a. flavin adenine dinucleotide
   b. vitamin A
   c. biotin
6. What is the function of each vitamin or coenzyme?
   a. vitamin K
   b. pyridoxal phosphate
   c. tetrahydrofolate

## Answers

1. a. fat soluble
   b. water soluble
   c. water soluble
3. a. vitamin $B_6$ or pyridoxine
   b. vitamin $B_2$ or riboflavin
   c. pantothenic acid
   d. vitamin $B_3$ or niacin
5. a. needed by enzymes that catalyze oxidation-reduction reactions in which two hydrogen atoms are transferred
   b. needed for the formation of vision pigments
   c. needed by enzymes that catalyze carboxylation reactions

# 18.9: Enzyme Cofactors and Vitamins

## Concept Review Exercises

1. What are the characteristics of an irreversible inhibitor?
2. In what ways does a competitive inhibitor differ from a noncompetitive inhibitor?

## Answers

1. It inactivates an enzyme by bonding covalently to a particular group at the active site.
2. A competitive inhibitor structurally resembles the substrate for a given enzyme and competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site and can bind to either the free enzyme or the enzyme-substrate complex.

## Exercises

1. What amino acid is present in the active site of all enzymes that are irreversibly inhibited by nerve gases such as DIFP?
2. Oxaloacetate (OOCCH2COCOO) inhibits succinate dehydrogenase. Would you expect oxaloacetate to be a competitive or noncompetitive inhibitor? Explain.

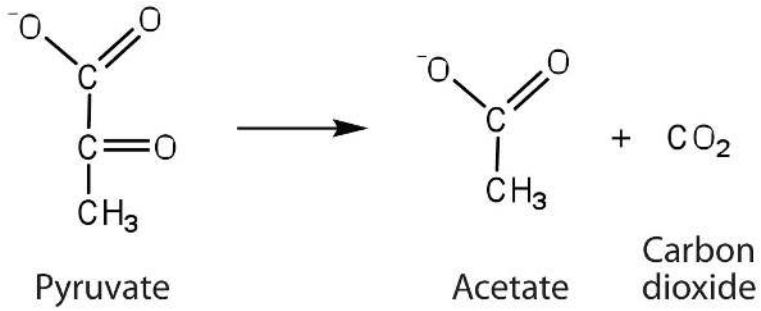
## Answer

1. serine

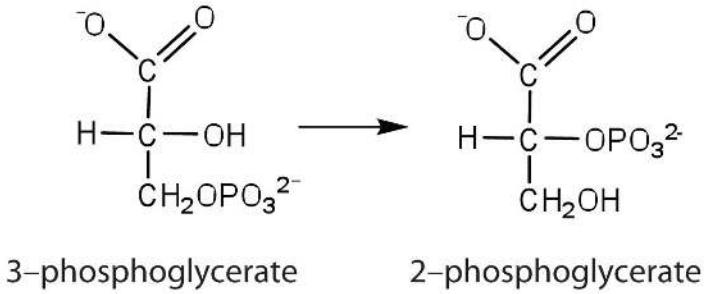
## Additional Exercises

1. Draw the structure of the amino acid γ-aminobutyric acid (GABA). Would you expect to find GABA in the amino acid sequence of a protein? Explain.
2. Draw the structure of the amino acid homocysteine (R group = $CH_2CH_2SH$). Would you expect to find homocysteine in the amino acid sequence of a protein? Justify your answer.
3. Write equations to show how leucine can act as a buffer (that is, how it can neutralize added acid or base).

4. Write equations to show how isoleucine can act as a buffer (that is, how it can neutralize added acid or base).
5. Glutathione (γ-glutamylcysteinylglycine) is a tripeptide found in all cells of higher animals. It contains glutamic acid joined in an unusual peptide linkage involving the carboxyl group of the R group (known as γ-carboxyl group), rather than the usual carboxyl group (the α-carboxyl group). Draw the structure of glutathione.
6. Draw the structure of the pentapeptide whose sequence is arg-his-gly-leu-asp. Identify which of the amino acids have R groups that can donate or gain hydrogen ions.
7. Bradykinin is a peptide hormone composed of nine amino acids that lowers blood pressure. Its primary structure is arg-pro-pro-gly-phe-ser-pro-phe-arg. Would you expect bradykinin to be positively charged, negatively charged, or neutral at a pH of 6.0? Justify your answer.
8. One of the neurotransmitters involved in pain sensation is a peptide called substance P, which is composed of 11 amino acids and is released by nerve-cell terminals in response to pain. Its primary structure is arg-pro-lys-pro-gln-gln-phe-phe-gly-leu-met. Would you expect this peptide to be positively charged, negatively charged, or neutral at a pH of 6.0? Justify your answer.
9. Carbohydrates are incorporated into *glycoproteins*. Would you expect the incorporation of sugar units to increase or decrease the solubility of a protein? Justify your answer.
10. Some proteins have phosphate groups attached through an ester linkage to the OH groups of serine, threonine, or tyrosine residues to form *phosphoproteins*. Would you expect the incorporation of a phosphate group to increase or decrease the solubility of a protein? Justify your answer.
11. Refer to Table 18.5 and determine how each enzyme would be classified.
    a. the enzyme that catalyzes the conversion of ethanol to acetaldehyde
    b. the enzyme that catalyzes the breakdown of glucose 6-phosphate to glucose and inorganic phosphate ion (water is also a reactant in this reaction)
12. Refer to Table 18.5 and determine how each enzyme would be classified.
    a. the enzyme that catalyzes the removal of a carboxyl group from pyruvate to form acetate

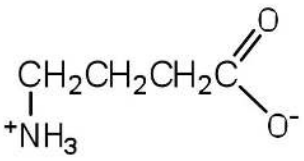



    b. the enzyme that catalyzes the rearrangement of 3-phosphoglycerate to form 2-phosphoglycerate



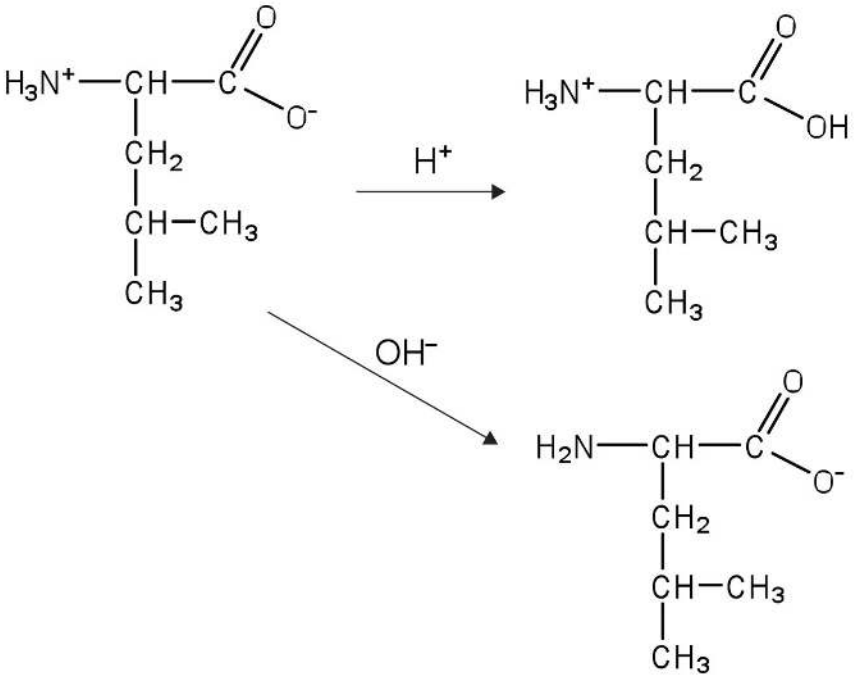
13. The enzyme lysozyme has an aspartic acid residue in the active site. In acidic solution, the enzyme is inactive, but activity increases as the pH rises to around 6. Explain why.
14. The enzyme lysozyme has a glutamic acid residue in the active site. At neutral pH (6–7), the enzyme is active, but activity decreases as the pH rises. Explain why.
15. The activity of a purified enzyme is measured at a substrate concentration of 1.0 μM and found to convert 49 μmol of substrate to product in 1 min. The activity is measured at 2.0 μM substrate and found to convert 98 μmol of substrate to product/minute.
    a. When the substrate concentration is 100 μM, how much substrate would you predict is converted to product in 1 min? What if the substrate concentration were increased to 1,000 μM (1.0 mM)?
    b. The activities actually measured are 676 μmol product formed/minute at a substrate concentration of 100 μM and 698 μmol product formed/minute at 1,000 μM (1.0 mM) substrate. Is there any discrepancy between these values and those you predicted in Exercise 15a? Explain.
16. A patient has a fever of 39°C. Would you expect the activity of enzymes in the body to increase or decrease relative to their activity at normal body temperature (37°C)?
17. Using your knowledge of factors that influence enzyme activity, describe what happens when milk is pasteurized.

## Answers



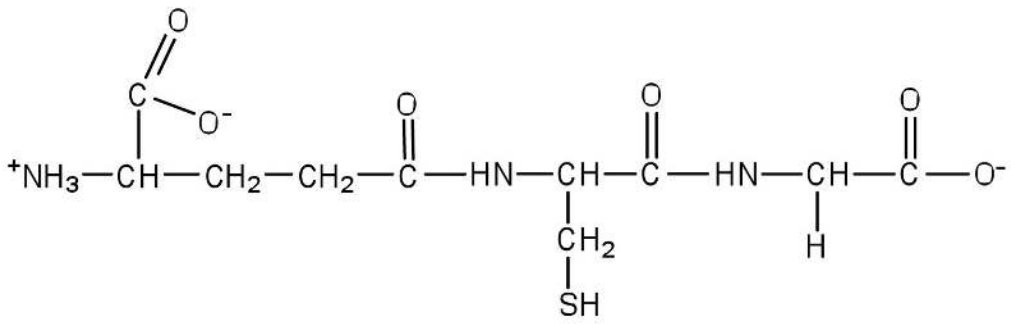
1.

This amino acid would not be found in proteins because it is not an α-amino acid.



3.

5.



7. Bradykinin would be positively charged; all of the amino acids, except for arginine, have R groups that do not become either positively or negatively charged. The two arginines are R groups that are positively charged at neutral pH, so the peptide would have an overall positive charge.

9. Carbohydrates have many OH groups attached, which can engage in hydrogen bonding with water, which increases the solubility of the proteins.

11.

a. oxidoreductase
b. hydrolase

13. The enzyme is active when the carboxyl group in the R group of aspartic acid does not have the hydrogen attached (forming $COO^-$); the hydrogen is removed when the pH of the solution is around pH 6 or higher.

15.

a. at 100 µM, you would predict that the rate would increase 100 times to 4,900 µmol of substrate to product in 1 min; at 1.0 mM, you would predict an increase to 49,000 µmol of substrate to product in 1 min.
b. There is a great discrepancy between the predicted rates and actual rates; this occurs because the enzyme becomes saturated with substrate, preventing a further increase in the rate of the reaction (the reaction is no longer linear with respect to substrate concentration because it is at very low concentrations).

17. When milk is pasteurized, it is heated to high temperatures. These high temperatures denature the proteins in bacteria, so they cannot carry out needed functions to grow and multiply.

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# 15.S: Amino Acids, Proteins, and Enzymes (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

A **protein** is a large biological polymer synthesized from **amino acids**, which are carboxylic acids containing an α-amino group. Proteins have a variety of important roles in living organisms, yet they are made from the same 20 L-amino acids. About half of these amino acids, the **essential amino acids**, cannot be synthesized by the human body and must be obtained from the diet. In the solid state and in neutral solutions, amino acids exist as **zwitterions**, species that are charged but electrically neutral. In this form, they behave much like inorganic salts. Each amino acid belongs to one of four classes depending on the characteristics of its R group or amino acid side chain: nonpolar, polar but neutral, positively charged, and negatively charged. Depending on the conditions, amino acids can act as either acids or bases, which means that proteins act as buffers. The pH at which an amino acid exists as the zwitterion is called the **isoelectric point (pI)**.

The amino acids in a protein are linked together by **peptide bonds**. Protein chains containing 10 or fewer amino acids are usually referred to as **peptides**, with a prefix such as di- or tri- indicating the number of amino acids. Chains containing more than 50 amino acid units are referred to as *proteins* or **polypeptides**. Proteins are classified globular or fibrous, depending on their structure and resulting solubility in water. **Globular proteins** are nearly spherical and are soluble in water; **fibrous proteins** have elongated or fibrous structures and are not soluble in water.

Protein molecules can have as many as four levels of structure. The **primary structure** is the sequence of amino acids in the chain. The **secondary structure** is the arrangement of adjacent atoms in the peptide chain; the most common arrangements are α-helices or β-pleated sheets. The **tertiary structure** is the overall three-dimensional shape of the molecule that results from the way the chain bends and folds in on itself. Proteins that consist of more than one chain have **quaternary structure**, which is the way the multiple chains are packed together.

Four types of intramolecular and intermolecular forces contribute to secondary, tertiary, and quaternary structure: (1) **hydrogen bonding** between an oxygen or a nitrogen atom and a hydrogen atom bound to an oxygen atom or a nitrogen atom, either on the same chain or on a neighboring chain; (2) **ionic bonding** between one positively charged side chain and one negatively charged side chain; (3) **disulfide linkages** between cysteine units; and (4) **dispersion forces** between nonpolar side chains.

Because of their complexity, protein molecules are delicate and easy to disrupt. A *denatured* protein is one whose conformation has been changed, in a process called **denaturation**, so that it can no longer do its physiological job. A variety of conditions, such as heat, ultraviolet radiation, the addition of organic compounds, or changes in pH can denature a protein.

An **enzyme** is an organic catalyst produced by a living cell. Enzymes are such powerful catalysts that the reactions they promote occur rapidly at body temperature. Without the help of enzymes, these reactions would require high temperatures and long reaction times.

The molecule or molecules on which an enzyme acts are called its **substrates**. An enzyme has an **active site** where its substrate or substrates bind to form an enzyme-substrate complex. The reaction occurs, and product is released:

$$E + S \rightarrow E\text{–}S \rightarrow E + P$$

The original **lock-and-key model** of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer **induced-fit model** describes the enzyme active site as changing its conformation after binding to the substrate.

Most enzymes have maximal activity in a narrow pH range centered on an **optimum pH**. In this pH range, the enzyme is correctly folded, and catalytic groups in the active site have the correct charge (positive, negative, or neutral). For most enzymes, the optimum pH is between 6 and 8.

Substances that interfere with enzyme function are called inhibitors. An **irreversible inhibitor** inactivates enzymes by forming covalent bonds to the enzyme, while a **reversible inhibitor** inactivates an enzyme by a weaker, noncovalent interaction that is easier to disrupt. A **competitive inhibitor** is a reversible inhibitor that is structurally similar to the substrate and binds to the active site. When the inhibitor is bound, the substrate is blocked from the active site and no reaction occurs. Because the binding of such

an inhibitor is reversible, a high substrate concentration will overcome the inhibition because it increases the likelihood of the substrate binding. A **noncompetitive inhibitor** binds reversibly at a site distinct from the active site. Thus, it can bind to either the enzyme or the enzyme-substrate complex. The inhibitor changes the conformation of the active site so that the enzyme cannot function properly. Noncompetitive inhibitors are important in **feedback inhibition**, in which the amount of product produced by a series of reactions is carefully controlled. The final product in a series of reactions acts as a noncompetitive inhibitor of the initial enzyme.

Simple enzymes consist entirely of one or more amino acid chains. Complex enzymes are composed of one or more amino acid chains joined to **cofactors**—inorganic ions or organic **coenzymes**. **Vitamins** are organic compounds that are essential in very small amounts for the maintenance of normal metabolism and generally cannot be synthesized at adequate levels by the body. Vitamins are divided into two broad categories: *fat-soluble* vitamins and *water-soluble* vitamins. Many of the water-soluble vitamins are used for the synthesis of coenzymes.

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# CHAPTER OVERVIEW

## 16: Quantities in Chemical Reactions

So far, we have talked about chemical reactions in terms of individual atoms and molecules. Although this works, most of the reactions occurring around us involve much larger amounts of chemicals. Even a tiny sample of a substance will contain millions, billions, or a hundred billion billions of atoms and molecules. How do we compare amounts of substances to each other in chemical terms when it is so difficult to count to a hundred billion billion? Actually, there are ways to do this, which we will explore in this chapter. In doing so, we will increase our understanding of stoichiometry, which is the study of the numerical relationships between the reactants and the products in a balanced chemical reaction.


16.1: Prelude to Quantities in Chemical Reactions
16.2: Atomic and Molar Masses
16.3: Mole-Mass Conversions
16.4: The Mole
16.5: An Introduction to Stoichiometry
16.6: Mole-Mole Relationships in Chemical Reactions
16.7: Mole-Mass and Mass-Mass Problems
16.8: Theoretical Yield and Percent Yield


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# 16.1: Prelude to Quantities in Chemical Reactions

> *When the disengaged gasses are carefully examined, they are found to weigh **113.7 grs.**; these are of two kinds, viz. **144 cubical inches** of carbonic acid gas, weighing **100 grs.** and **380 cubical inches** of a very light gas, weighing only **13.7 grs.**…and, when the water which has passed over into the bottle [labeled] H is carefully examined, it is found to have lost **85.7 grs.** of its weight. Thus, in this experiment, **85.7 grs.** of water, joined to **28 grs.** of charcoal, have combined in such a way as to form **100 grs.** of carbonic acid, and **13.7 grs.** of a particular gas capable of being burnt. (Bold emphasis added.)*

In this paragraph from the *Elements of Chemistry*, Antoine Lavoisier (1743–94) is explaining an experiment in which he was trying to demonstrate that water is not an element but instead is composed of hydrogen (the gas “capable of being burnt”) and oxygen. This is a historical account of a groundbreaking experiment and illustrates the importance of amounts in chemistry. Lavoisier was pointing out that the initial total mass of water and charcoal, 85.7 g plus 28 g, equals the final total mass of carbonic acid and the particular gas, 100 g plus 13.7 g. In this way, he was illustrating the law of conservation of matter. It is another way of saying that *amounts matter*.

Amounts do matter and in a variety of circumstances. The chapter-opening essay in Chapter 1 tells the story of a nurse who mistakenly read “2–3 mg” as “23 mg” and administered the higher and potentially fatal dose of morphine to a child. Food scientists who work in test kitchens must keep track of specific amounts of ingredients as they develop new products for us to eat. Quality control technicians measure amounts of substances in manufactured products to ensure that the products meet company or government standards. Supermarkets routinely weigh meat and produce and charge consumers by the ounce or the pound.

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# 16.2: Atomic and Molar Masses

**Learning Objectives**

- To learn how the masses of moles of atoms and molecules are expressed.

Now that we have introduced the mole and practiced using it as a conversion factor, we ask the obvious question: why is the mole *that particular* number of things? Why is it $6.022 \times 10^{23}$ and not $1 \times 10^{23}$ or even $1 \times 10^{20}$?

The number in a mole, Avogadro's number, is related to the relative sizes of the **atomic mass unit** and **gram mass units**. Whereas one hydrogen atom has a mass of approximately 1 u, **1 mol of H atoms** has a mass of approximately **1 *gram***. And whereas one sodium atom has an approximate mass of 23 u, 1 mol of Na atoms has an approximate mass of 23 *grams*.

*One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units.* The numbers in the periodic table that we identified as the atomic masses of the atoms not only tell us the mass of one atom in u but also tell us the mass of 1 mol of atoms in grams.

> One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units.

**Example 16.2.1: Moles to Mass Conversion with Elements**

What is the mass of each quantity?

a. 1 mol of Al atoms
b. 2 mol of U atoms

**Solution**

a. One mole of Al atoms has a mass in grams that is numerically equivalent to the atomic mass of aluminum. The periodic table shows that the atomic mass (rounded to two decimal points) of Al is 26.98, so 1 mol of Al atoms has a mass of 26.98 g.
b. According to the periodic table, 1 mol of U has a mass of 238.0 g, so the mass of 2 mol is twice that, or 476.0 g.

**Exercise 16.2.1: Moles to Mass Conversion with Elements**

What is the mass of each quantity?

a. 1 mol of Au atoms
b. 5 mol of Br atoms

**Answer a**

197.0 g

**Answer b**

5 mol Br atoms x 79.90 g/mol = 399.5 g

The mole concept can be extended to masses of formula units and molecules as well. The mass of 1 mol of molecules (or formula units) in grams is numerically equivalent to the mass of one molecule (or formula unit) in atomic mass units. For example, a single molecule of $O_2$ has a mass of 32.00 u, and 1 mol of $O_2$ molecules has a mass of 32.00 g. As with atomic mass unit–based masses, to obtain the mass of 1 mol of a substance, we simply sum the masses of the individual atoms in the formula of that substance. The mass of 1 mol of a substance is referred to as its **molar mass**, whether the substance is an element, an ionic compound, or a covalent compound.

## Example 16.2.2: Moles to Mass Conversion with Compounds

What is the mass of 1 mol of each substance?

a. NaCl
b. bilirubin ($C_{33}H_{36}N_4O_6$), the principal pigment present in bile (a liver secretion)

### Solution a

1. Summing the molar masses of the atoms in the NaCl formula unit gives

Solutions to Example 6.2.2, Summing the molar masses of the atoms in the NaCl formula unit gives

| | |
|---|---|
| **1 Na molar mass:** | 22.99 g |
| **1 Cl molar mass:** | 35.45 g |
| **Total:** | 58.44 g |

The mass of 1 mol of NaCl is 58.44 g.

### Solution b

Multiplying the molar mass of each atom by the number of atoms of that type in bilirubin's formula and adding the results, we get

Solutions to Example 6.2.2, Multiplying the molar mass of each atom by the number of atoms of that type in bilirubin's formula and adding the results, we get

| | | |
|---|---|---|
| **33 C molar mass:** | 33 × 12.01 g | 396.33 g |
| **36 H molar mass:** | 36 × 1.01 = | 36.36 g |
| **4 N molar mass:** | 4 × 14.01 = | 56.04 g |
| **6 O molar mass:** | 6 × 16.00 = | 96.00 g |
| **Total:** | | 584.73 g |

The mass of 1 mol of bilirubin is 584.73 g.

## Exercise 16.2.2: Moles to Mass Conversion with Compounds

What is the mass of 1 mol of each substance?

a. barium sulfate ($BaSO_4$), used to take X rays of the gastrointestional tract
b. adenosine ($C_{10}H_{13}N_5O_4$), a component of cell nuclei crucial for cell division

**Answer a**

233.36 g

**Answer b**

267.28 g

Be careful when counting atoms. In formulas with polyatomic ions in parentheses, the subscript outside the parentheses is applied to every atom inside the parentheses. For example, the molar mass of $Ba(OH)_2$ requires the sum of 1 mass of Ba, 2 masses of O, and 2 masses of H:

The molar mass of Ba(OH)2 requires the sum of 1 mass of Ba, 2 masses of O, and 2 masses of H:

| | | |
|---|---|---|
| **1 Ba molar mass:** | 1 × 137.3 g = | 137.3 g |
| **2 O molar mass:** | 2 × 16.00 g = | 32.00 g |
| **2 H molar mass:** | 2 × 1.01 g = | 2.02 g |
| **Total:** | | 171.32 g |

Because molar mass is defined as the mass for 1 mol of a substance, we can refer to molar mass as grams per mole (g/mol). The division sign (/) implies “per,” and “1” is implied in the denominator. Thus, the molar mass of bilirubin can be expressed as 584.73 g/mol, which is read as “five hundred eighty four point seventy three grams per mole.”

## Key Takeaway

- The mass of moles of atoms and molecules is expressed in units of grams.

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# 16.3: Mole-Mass Conversions

**Learning Objectives**

- To convert quantities between mass units and mole units.

A previous Example stated that the mass of 2 mol of U is twice the molar mass of uranium. Such a straightforward exercise does not require any formal mathematical treatment. Many questions concerning mass are not so straightforward, however, and require some mathematical manipulations.

The simplest type of manipulation using molar mass as a conversion factor is a mole-mass conversion (or its reverse, a mass-mole conversion). In such a conversion, we use the molar mass of a substance as a conversion factor to convert mole units into mass units (or, conversely, mass units into mole units).

We also established that 1 mol of Al has a mass of 26.98 g (Example **16.3.1**). 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:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \quad \text{and} \quad \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

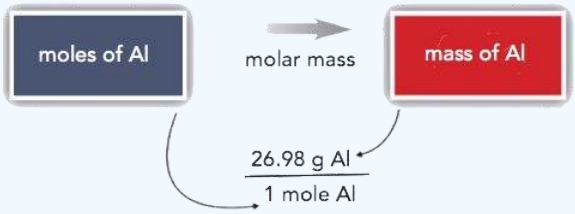
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do "by eye."

**Example 16.3.1**

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 16.3.1**

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 **16.3.1** is a chart for determining what conversion factor is needed, and Figure **16.3.2** is a flow diagram for the steps needed to perform a conversion.

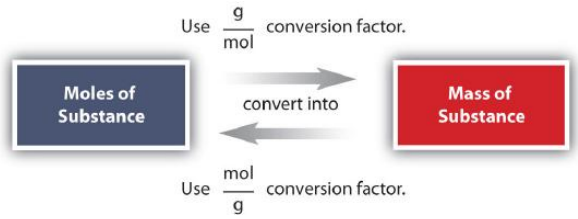



Figure **16.3.1** A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

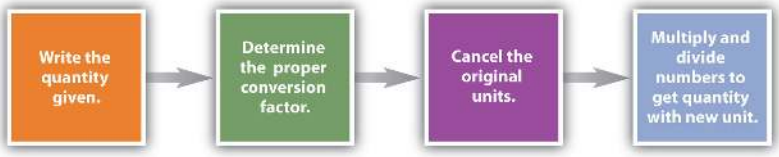



Figure **16.3.2** A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

## Example 16.3.2

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:

Solutions to Example 6.3.2

| | | |
|---|---|---|
| **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 mol bilirubin = 584.73 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 **16.3.2**:

$$0.00655\ \text{mol bilirubin} \times \frac{584.73\ \text{g bilirubin}}{\text{mol bilirubin}} = 3.83\ \text{g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

## Exercise 16.3.2

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 **16.3.1**: Essential Minerals and their Composition in Humans

| Mineral | Male (age 19–30 y) | | Female (age 19–30 y) | |
|---|---|---|---|---|
| Ca | 1,000 mg | 0.025 mol | 1,000 mg | 0.025 mol |
| Cr | 35 µg | $6.7 \times 10^{-7}$ mol | 25 µg | $4.8 \times 10^{-7}$ mol |
| Cu | 900 µg | $1.4 \times 10^{-5}$ mol | 900 µg | $1.4 \times 10^{-5}$ mol |
| F | 4 mg | $2.1 \times 10^{-4}$ mol | 3 mg | $1.5 \times 10^{-4}$ mol |
| I | 150 µg | $1.2 \times 10^{-6}$ mol | 150 µg | $1.2 \times 10^{-6}$ mol |
| Fe | 8 mg | $1.4 \times 10^{-4}$ mol | 18 mg | $3.2 \times 10^{-4}$ mol |
| K | 3,500 mg | $9.0 \times 10^{-2}$ mol | 3,500 mg | $9.0 \times 10^{-2}$ mol |
| Mg | 400 mg | $1.6 \times 10^{-2}$ mol | 310 mg | $1.3 \times 10^{-2}$ mol |
| Mn | 2.3 mg | $4.2 \times 10^{-5}$ mol | 1.8 mg | $3.3 \times 10^{-5}$ mol |
| Mo | 45 mg | $4.7 \times 10^{-7}$ mol | 45 mg | $4.7 \times 10^{-7}$ mol |
| Na | 2,400 mg | $1.0 \times 10^{-1}$ mol | 2,400 mg | $1.0 \times 10^{-1}$ mol |
| P | 700 mg | $2.3 \times 10^{-2}$ mol | 700 mg | $2.3 \times 10^{-2}$ mol |
| Se | 55 µg | $7.0 \times 10^{-7}$ mol | 55 µg | $7.0 \times 10^{-7}$ mol |
| Zn | 11 mg | $1.7 \times 10^{-4}$ mol | 8 mg | $1.2 \times 10^{-4}$ mol |

Table **16.3.1** 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*).

## Key Takeaway

- It is possible to convert between moles of material and mass of material.

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# 16.4: The Mole

**Learning Objectives**

- To define the mole unit.

Figure **16.4.1** shows that we need 2 hydrogen atoms and 1 oxygen atom to make 1 water molecule. If we want to make 2 water molecules, we will need 4 hydrogen atoms and 2 oxygen atoms. If we want to make 5 molecules of water, we need 10 hydrogen atoms and 5 oxygen atoms. The ratio of atoms we will need to make any number of water molecules is the same: 2 hydrogen atoms to 1 oxygen atom.

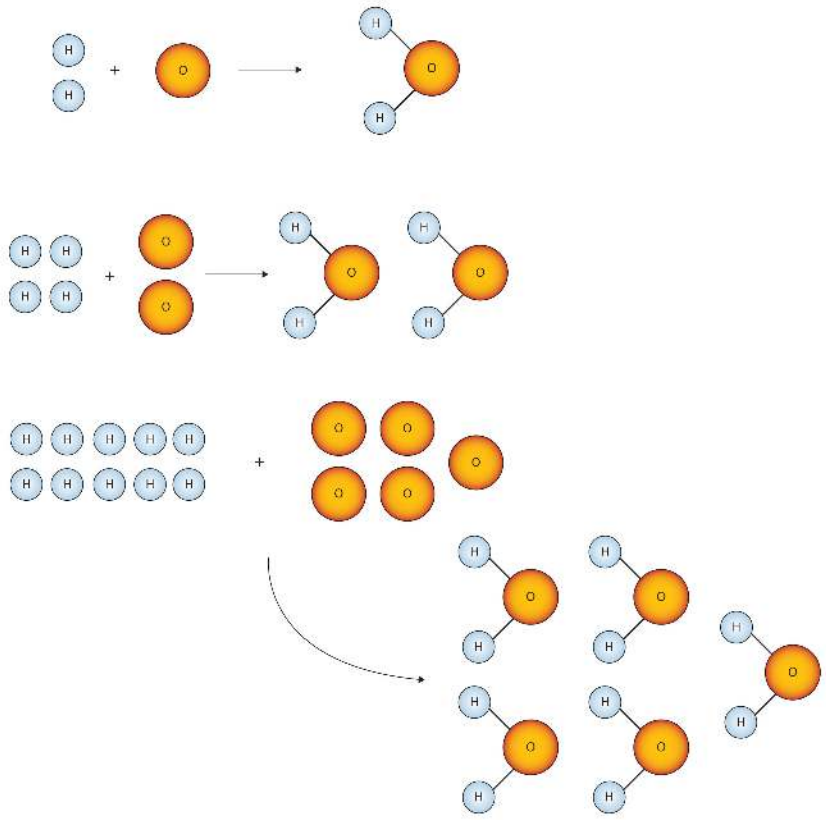


Figure **16.4.1** Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

One problem we have, however, is that it is extremely difficult, if not impossible, to organize atoms one at a time. As stated in the introduction, we deal with billions of atoms at a time. How can we keep track of so many atoms (and molecules) at a time? We do it by using mass rather than by counting individual atoms.

A hydrogen atom has a mass of approximately 1 u. An oxygen atom has a mass of approximately 16 u. The ratio of the mass of an oxygen atom to the mass of a hydrogen atom is therefore approximately 16:1.

If we have 2 atoms of each element, the ratio of their masses is approximately 32:2, which reduces to 16:1—the same ratio. If we have 12 atoms of each element, the ratio of their total masses is approximately (12 × 16):(12 × 1), or 192:12, which also reduces to 16:1. If we have 100 atoms of each element, the ratio of the masses is approximately 1,600:100, which again reduces to 16:1. As long as we have equal numbers of hydrogen and oxygen atoms, the ratio of the masses will always be 16:1.

The same consistency is seen when ratios of the masses of other elements are compared. For example, the ratio of the masses of silicon atoms to equal numbers of hydrogen atoms is always approximately 28:1, while the ratio of the masses of calcium atoms to equal numbers of lithium atoms is approximately 40:7.

So we have established that the masses of atoms are constant with respect to each other, as long as we have the same number of each type of atom. Consider a more macroscopic example. If a sample contains 40 g of Ca, this sample has the same number of atoms as there are in a sample of 7 g of Li. What we need, then, is a number that represents a convenient quantity of atoms so we can relate macroscopic quantities of substances. Clearly even 12 atoms are too few because atoms themselves are so small. We need a number that represents billions and billions of atoms.

Chemists use the term **mole** to represent a large number of atoms or molecules. Just as a dozen implies 12 things, a **mole** (abbreviated as ***mol***) represents **$6.022 \times 10^{23}$ things**. The number $6.022 \times 10^{23}$, called Avogadro's number after the 19th-century chemist Amedeo Avogadro, is the number we use in chemistry to represent macroscopic amounts of atoms and molecules. Thus, if we have $6.022 \times 10^{23}$ Na atoms, we say we have 1 mol of Na atoms. If we have 2 mol of Na atoms, we have $2 \times (6.022 \times 10^{23})$ Na atoms, or $1.2044 \times 10^{24}$ Na atoms. Similarly, if we have 0.5 mol of benzene ($C_6H_6$) molecules, we have $0.5 \times (6.022 \times 10^{23})$ $C_6H_6$ molecules, or $3.011 \times 10^{23}$ $C_6H_6$ molecules.

> A mole represents a very large number! If 1 mol of quarters were stacked in a column, it could stretch back and forth between Earth and the sun *6.8 billion* times.

Notice that we are applying the mole unit to different types of **chemical entities**. The word *mole* represents a number of things—$6.022 \times 10^{23}$ of them—but does not by itself specify what "they" are. The chemical entities can be ***atoms, molecules***, ***formula units*** and ***ions***. This specific information needs to be specified accurately. Most students find this confusing hence, we need to review the composition of elements, covalent and ionic compounds.

Most elements are made up of individual ***atoms,*** such as helium. However, some elements consist of ***molecules***, such as the diatomic elements, nitrogen, hydrogen, oxygen, etc. One mole of He consists of $6.022 \times 10^{23}$ He ***atoms*** but one mole of nitrogen contains $6.022 \times 10^{23}$ $N_2$ ***molecules***. The basic units of covalent (molecular) compounds are ***molecules*** as well. The molecules of "compounds" consist of different kinds of atoms while the molecules of "elements" consist of only one type of atom. For example, the molecules of ammonia ($NH_3$) consist of nitrogen and hydrogen atoms while $N_2$ molecules have N atoms only. Compounds that are ionic, like NaCl, are represented by ionic formulas. One mole of NaCl, for example, refers to $6.022 \times 10^{23}$ ***formula units*** of NaCl. And, one formula unit of NaCl consists of one sodium ***ion*** and one chloride ***ion***. Figure 6.1.2 summarizes the basic units of elements, covalent and ionic compounds

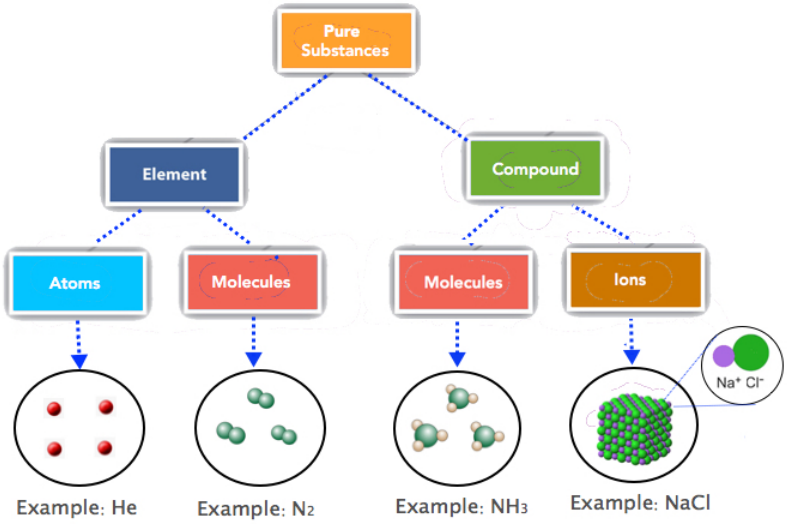



Figure **16.4.2**: The basic units of elements (atoms or molecules), covalent compounds (molecules) and ionic compounds (formula units of ions).

## Conversion Between Moles and Atoms, Molecules and Ions

Using our unit conversion techniques learned in Chapter 1, we can use the mole relationship and the chemical formula to convert back and forth between the moles and the number of chemical entities (atoms, molecules or ions).

Because 1 $N_2$ molecule contains 2 N atoms, 1 mol of $N_2$ molecules ($6.022 \times 10^{23}$ molecules) has 2 mol of N atoms. Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of ethanol ($C_2H_6O$), we can construct the following relationships (Table **16.4.1**):

Table **16.4.1**: Molecular Relationships

| 1 Molecule of $C_2H_6O$ Has | 1 Mol of $C_2H_6O$ Has | Molecular Relationships |
|---|---|---|
| 2 C atoms | 2 mol of C atoms | $\frac{2\ \text{mol C atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}$ or $\frac{1\ \text{mol } C_2H_6O\ \text{molecules}}{2\ \text{mol C atoms}}$ |
| 6 H atoms | 6 mol of H atoms | $\frac{6\ \text{mol H atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}$ or $\frac{1\ \text{mol } C_2H_6O\ \text{molecules}}{6\ \text{mol H atoms}}$ |
| 1 O atom | 1 mol of O atoms | $\frac{1\ \text{mol O atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}$ or $\frac{1\ \text{mol } C_2H_6O\ \text{molecules}}{1\ \text{mol O atoms}}$ |

The following example illustrates how we can use these relationships as conversion factors.

### Example 16.4.1

If a sample consists of 2.5 mol of ethanol ($C_2H_6O$), how many moles of carbon atoms, hydrogen atoms, and oxygen atoms does it have?

#### Solution

Using the relationships in Table **16.4.1**, we apply the appropriate conversion factor for each element:

$$2.5\ \text{mol } C_2H_6O\ \text{molecules} \times \underbrace{\frac{2\ \text{mol C atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}}_{\text{conversion factor}} = 5.0\ \text{mol C atoms}$$

Note how the unit *mol $C_2H_6O$ molecules* cancels algebraically. Similar equations can be constructed for determining the number of H and O atoms:

$$2.5\ \text{mol } C_2H_6O\ \text{molecules} \times \frac{6\ \text{mol H atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}} = 15\ \text{mol H atoms}$$

$$2.5\ \text{mol } C_2H_6O\ \text{molecules} \times \frac{1\ \text{mol O atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}} = 2.5\ \text{mol O atoms}$$

### Exercise 16.4.1

If a sample contains 6.75 mol of $Na_2SO_4$, how many moles of sodium atoms, sulfur atoms, and oxygen atoms does it have?

**Answer**

13.5 mol Na, 6.75 mol S and 27 mol O.

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. For example, if we are dealing with element X, the mole relationship is expressed as follows:

$$1\ \text{mol X} = 6.022 \times 10^{23}\ \text{X atoms}$$

We can convert this relationship into two possible conversion factors shown below:

$$\frac{1\ \text{mol X}}{6.022 \times 10^{23}\ \text{X atoms}} \text{ or } \frac{6.022 \times 10^{23}\ \text{X atoms}}{1\ \text{mol X}}$$

If the number of "atoms of element X" is given, we can convert it into "moles of X" by multiplying the given value with the conversion factor at the left. However, if the number of "mol of X" is given, the appropriate conversion factor to use is the one at

the right.

If we are dealing with a molecular compound (such as $C_4H_{10}$), the mole relationship is expressed as follows:

$$1 \text{ mol } C4H10 = 6.022 \times 10^{23} \text{ } C4H10 \text{ molecules}$$

If working with ionic compounds (such as NaCl), the mole relationship is expressed as follows:

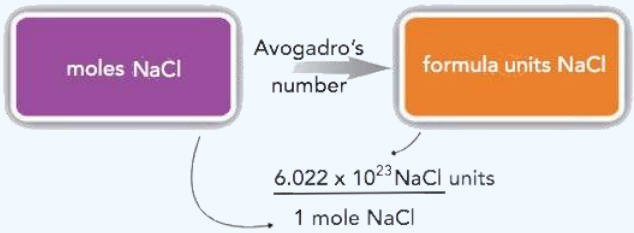
$$1 \text{ mol NaCl} = 6.022 \times 10^{23} \text{ NaCl formula units}$$

### Example 16.4.2

How many formula units are present in 2.34 mol of NaCl? How many ions are in 2.34 mol?

**Solution**

Typically in a problem like this, we start with what we are given and apply the appropriate conversion factor. Here, we are given a quantity of 2.34 mol of NaCl, to which we can apply the definition of a **mole as a conversion factor**:




$$2.34 \text{ mol NaCl} \times \frac{6.022 \times 10^{23} \text{ NaCl units}}{1 \text{ mol NaCl}} = 1.41 \times 10^{24} \text{ NaCl units}$$

Because there are two ions per formula unit, there are

$$1.41 \times 10^{24} \text{ NaCl units} \times \frac{2 \text{ ions}}{\text{NaCl units}} = 2.82 \times 10^{24} \text{ ions}$$

in the sample.

### Exercise 16.4.2

How many molecules are present in 16.02 mol of $C_4H_{10}$? How many atoms are in 16.02 mol?

**Answer**

9.647 x $10^{24}$molecules, 1.351 x $10^{26}$ atoms.

## Key Takeaway

- A mole is $6.022 \times 10^{23}$ things.

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# 16.5: An Introduction to Stoichiometry

*Stoichiometry*… what a wonderful word! It sounds so complex and so *chemical*. In fact, it's a fairly simple concept; **stoichiometry** is the relationship between the molar masses of chemical reactants and products in a given chemical reaction. In Chapter 5 we learned to balance chemical equations by inserting numerical coefficients in front of reactants or products so that there were the same number and types of atoms on each side of the equation. Thus, in the reaction between sodium metal and chlorine gas, the balanced chemical equation is:

$$2\,Na\,(s) + Cl_2\,(g) \rightarrow 2\,NaCl\,(s)$$

This equation tells us that two atoms of sodium react with one molecule of chlorine gas to give two sodium chlorides. The coefficients in front of the sodium and the sodium chloride are called the **stoichiometric coefficients** for this reaction. If we were to totally react a single molecule of chlorine gas in this reaction, this stoichiometry tells us that two atoms of sodium (atomic mass 22.99) having a total mass of 45.98 amu, would react with one molecule of chlorine gas (having a mass 70.90 amu) to give two sodium chlorides (formula mass 137.94), for a total of 275.9 amu of product. Because chemists usually don't speak of chemical reactions in terms of individual atoms or molecules, it is much more common to describe the stoichiometry of a reaction in terms of grams of reactants and products, or more conveniently in terms of moles. **Molar stoichiometry** is simply the expression of the coefficients of a reaction in terms of moles of reactants and products.

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# 16.6: Mole-Mole Relationships in Chemical Reactions

**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

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4\,H_2 + 2\,O_2 \longrightarrow 4\,H_2O$$

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22\,H_2 + 11\,O_2 \longrightarrow 22\,H_2O$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$

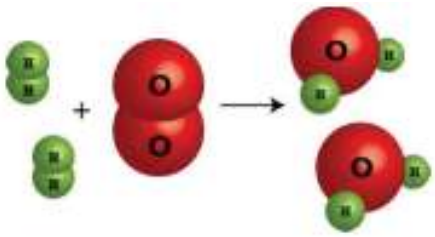
These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But $6.022 \times 10^{23}$ is 1 mol, while $12.044 \times 10^{23}$ is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ \text{mol}\ \ H_2 + 1\ \ \text{mol}\ \ O_2 \longrightarrow 2\ \text{mol}\ \ H_2O$$

We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level but also in terms of molar amounts of reactants and products.* Thus, we can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.”



2 molecules $H_2$ 1 molecule $O_2$ 2 molecules $H_2O$

2 moles $H_2$ 1 mole $O_2$ 2 moles $H_2O$

2 x 2.02 g=4.04 g $H_2$ 32.0 g $O_2$ 2 x 18.02 g=36.04 g $H_2O$

Figure **16.6.1**: This representation of the production of water from oxygen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

By the same token, the ratios we constructed to describe molecules reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following

ratios:

$$\frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ O_2}\ \text{or}\ \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2}$$

$$\frac{2\ \text{mol}\ H_2O}{1\ \text{mol}\ O_2}\ \text{or}\ \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2O}$$

$$\frac{2\ \text{mol}\ H_2}{2\ \text{mol}\ H_2O}\ \text{or}\ \frac{2\ \text{mol}\ H_2O}{2\ \text{mol}\ H_2}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called ***stoichiometry*.** The ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products is called the **stoichiometric factor.**

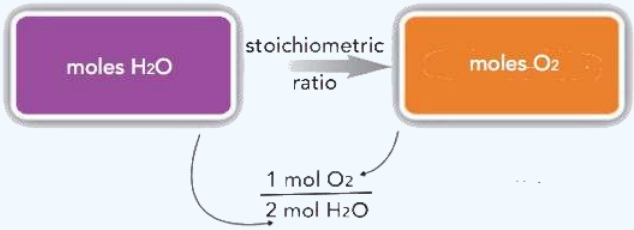
### Example 16.6.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of $H_2O$? The balanced equation is as follows:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

#### Solution

Because we are dealing with quantities of $H_2O$ and $O_2$, we will use the **stoichiometric ratio** that relates those two substances. Because we are given an amount of $H_2O$ and want to determine an amount of $O_2$, we will use the ratio that has $H_2O$ in the denominator (so it cancels) and $O_2$ in the numerator (so it is introduced in the answer). Thus,




$$27.6\ \text{mol}\ H_2O \times \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2O} = 13.8\ \text{mol}\ O_2$$

To produce 27.6 mol of $H_2O$, 13.8 mol of $O_2$ react.

### Exercise 16.6.1

Using $2H_2 + O_2 \rightarrow 2H_2O$, how many moles of hydrogen react with 3.07 mol of oxygen to produce $H_2O$?

**Answer**

$$3.07\ \text{mol}\ O_2 \times \frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ O_2} = 6.14\ \text{mol}\ H_2$$

## Key Takeaway

- The balanced chemical reaction can be used to determine molar relationships between substances.

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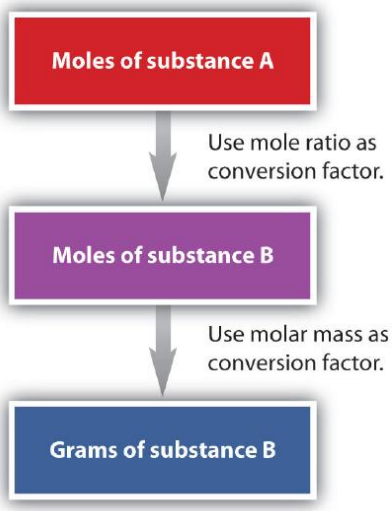
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# 16.7: Mole-Mass and Mass-Mass Problems

**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

$$\mathrm{Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3}$$

If we have 3.59 mol of $Fe_2O_3$, how many grams of $SO_3$ can react with it? Using the mole-mass calculation sequence, we can determine the required mass of $SO_3$ in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of $SO_3$ needed. Then using the molar mass of $SO_3$ as a conversion factor, we determine the mass that this number of moles of $SO_3$ has.

The first step resembles the exercises we did in Section 6.4. As usual, we start with the quantity we were given:

$$\mathrm{3.59\ mol\ Fe_2O_3 \times \frac{3\ mol\ SO_3}{1\ mol\ Fe_2O_3} = 10.77\ mol\ SO_3}$$

The mol $Fe_2O_3$ units cancel, leaving mol $SO_3$ unit. Now, we take this answer and convert it to grams of $SO_3$, using the molar mass of $SO_3$ as the conversion factor:

$$\mathrm{10.77\ mol\ SO_3 \times \frac{80.07\ g\ SO_3}{1\ mol\ SO_3} = 862.4\ g\ SO_3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of $SO_3$ will react with 3.59 mol of $Fe_2O_3$. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:




$$3.59 \text{ mol } Fe_2O_3 \times \underbrace{\frac{3 \text{ mol } SO_3}{1 \text{ mol } Fe_2O_3}}_{\text{converts to moles of } SO_3} \times \underbrace{\frac{80.07 \text{ g } SO_3}{1 \text{ mol } SO_3}}_{\text{converts to grams of } SO_3} = 862.4 \text{ g } SO_3$$

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

### Example 16.7.1

How many grams of $CO_2$ are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation?

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

**Solution**

Our strategy will be to convert from moles of $HCl$ to moles of $CO_2$ and then from moles of $CO_2$ to grams of $CO_2$. We will need the molar mass of $CO_2$, which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of $CO_2$:

$$2.09 \text{ mol } HCl \times \underbrace{\frac{1 \text{ mol } CO_2}{2 \text{ mol } HCl}}_{\text{from the coefficients of the balanced equation}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 46.0 \text{ g } CO_2$$

The molar ratio between $CO_2$ and HCl comes from the balanced chemical equation.

### Exercise

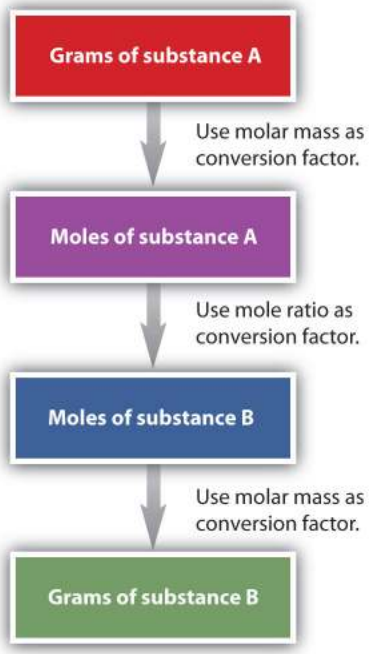
How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of $H_2O$ are reacted according to this balanced chemical equation?

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2$$

**Answer**

$$17.3 \text{ mol } H_2O \times \frac{1 \text{ mol } C_6H_{12}O_6}{6 \text{ mol } H_2O} \times \frac{180.18 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6} = 520 \text{ g } C_6H_{12}O_6$$

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 16.7.2: Chlorination of Carbon

Methane can react with elemental chlorine to make carbon tetrachloride ($CCl_4$). The balanced chemical equation is as follows:

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

How many grams of HCl are produced by the reaction of 100.0 g of $CH_4$?

#### 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:

$$100.0\ g\ CH_4 \times \frac{1\ mol\ CH_4}{16.05\ g\ CH_4} = 6.231\ mol\ CH_4$$

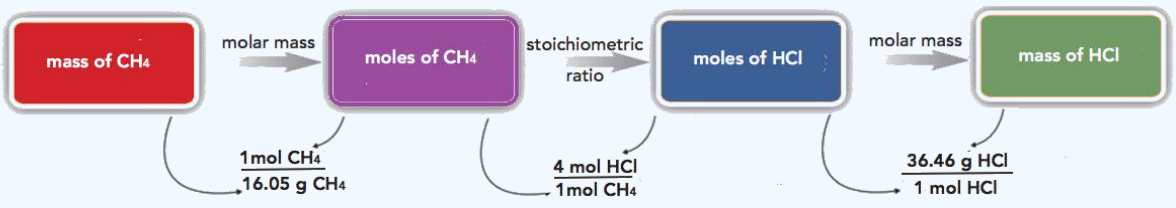
Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles $CCl_4$ and moles HCl and convert our first result into moles of HCl:

$$6.231\ mol\ CH_4 \times \frac{4\ mol\ HCl}{1\ mol\ CH_4} = 24.92\ mol\ HCl$$

Finally, we use the molar mass of HCl (36.46 g/mol) as a conversion factor to calculate the mass of 24.92 mol of HCl:

$$24.92\ mol\ HCl \times \frac{36.46\ g\ HCl}{1\ mol\ HCl} = 908.5\ g\ HCl$$

In each step, we have limited the answer to the proper number of significant figures. If desired, we can do all three conversions on a single line:





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$$100.0\ \text{g CH}_4 \times \frac{1\ \text{mol CH}_4}{16.05\ \text{g CH}_4} \times \frac{4\ \text{mol HCl}}{1\ \text{mol CH}_4} \times \frac{36.46\ \text{g HCl}}{1\ \text{mol HCl}} = 908.7\ \text{g HCl}$$

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 16.7.2: Oxidation of Propanal

The oxidation of propanal ($CH_3CH_2CHO$) to propionic acid ($CH_3CH_2COOH$) has the following chemical equation:

$$CH_3CH_2CHO + 2K_2Cr_2O_7 \rightarrow CH_3CH_2COOH + \text{other products}$$

How many grams of propionic acid are produced by the reaction of 135.8 g of $K_2Cr_2O_7$?

**Answer**

$$135.8\ \text{g K}_2\text{Cr}_2\text{O}_7 \times \frac{1\ \text{mol K}_2\text{Cr}_2\text{O}_7}{294.20\ \text{g K}_2\text{Cr}_2\text{O}_7} \times \frac{1\ \text{mol CH}_3\text{CH}_2\text{COOH}}{2\ \text{mol K}_2\text{Cr}_2\text{O}_7} \times \frac{74.09\ \text{g CH}_3\text{CH}_2\text{COOH}}{1\ \text{mol CH}_3\text{CH}_2\text{COOH}} = 17.10\ \text{g CH}_3\text{CH}_2\text{COOH}$$

### To Your Health: The Synthesis of Taxol

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

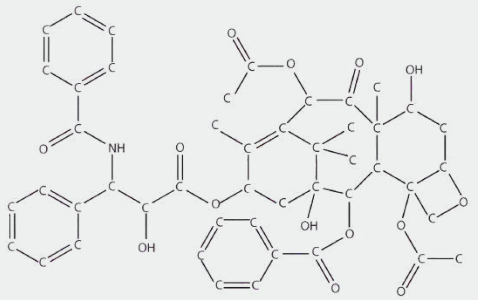



Figure 16.7.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

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.

## Key Takeaway

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

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# 16.8: Theoretical Yield and Percent Yield



Figure 16.8.1 (Public Domain; Linda Bartlett and the National Cancer Institute via Wikipedia)

## Can we save some money?

The world of pharmaceutical production is an expensive one. Many drugs have several steps in their synthesis and use costly chemicals. A great deal of research takes place to develop better ways to make drugs faster and more efficiently. Studying how much of a compound is produced in any given reaction is an important part of cost control.

## Percent Yield

Chemical reactions in the real world do not always go exactly as planned on paper. In the course of an experiment, many things will contribute to the formation of less product than would be predicted. Besides spills and other experimental errors, there are often losses due to an incomplete reaction, undesirable side reactions, etc. Chemists need a measurement that indicates how successful a reaction has been. This measurement is called the percent yield.

To compute the percent yield, it is first necessary to determine how much of the product should be formed based on stoichiometry. This is called the **theoretical yield**, the maximum amount of product that could be formed from the given amounts of reactants. The **actual yield** is the amount of product that is actually formed when the reaction is carried out in the laboratory. The **percent yield** is the ratio of the actual yield to the theoretical yield, expressed as a percentage:

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Percent yield is very important in the manufacture of products. Much time and money is spent improving the percent yield for chemical production. When complex chemicals are synthesized by many different reactions, one step with a low percent yield can quickly cause a large waste of reactants and unnecessary expense.

Typically, percent yields are understandably less than $100\%$ because of the reasons previously indicated. However, percent yields greater than $100\%$ are possible if the measured product of the reaction contains impurities that cause its mass to be greater than it actually would be if the product was pure. When a chemist synthesizes a desired chemical, he or she is always careful to purify the products of the reaction.

### Example 16.8.1: Calculating the Theoretical Yield and the Percent Yield

Potassium chlorate decomposes upon slight heating in the presence of a catalyst, according to the reaction below.

$$2KClO_3\,(s) \rightarrow 2KCl\,(s) + 3O_2\,(g)$$

In a certain experiment, $40.0\ g\ KClO_3$ is heated until it completely decomposes. What is the theoretical yield of oxygen gas? The experiment is performed, the oxygen gas is collected, and its mass is found to be $14.9\ g$. What is the percent yield for the reaction?

**Solution**

First, we will calculate the theoretical yield based on the stoichiometry.

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

**Known**

- Molar mass $KClO_3 = 122.55\ g/mol$
- Molar mass $O_2 = 32.00\ g/mol$

**Unknown**

- theoretical yield $O_2$ = ? g

Apply stoichiometry to convert from the mass of a reactant to the mass of a product:

$$g\ KClO_3 \rightarrow mol\ KClO_3 \rightarrow mol\ O_2 \rightarrow g\ O_2$$

***Step 2: Solve.***

$$40.0\ g\ KClO_3 \times \frac{1\ mol\ KClO_3}{122.55\ g\ KClO_3} \times \frac{3\ mol\ O_2}{2\ mol\ KClO_3} \times \frac{32.00\ g\ O_2}{1\ mol\ O_2} = 15.7\ g\ O_2$$

The theoretical yield of $O_2$ is $15.7\ g$.

***Step 3: Think about your result.***

The mass of oxygen gas must be less than the $40.0\ g$ of potassium chlorate that was decomposed.

Now we will use the actual yield and the theoretical yield to calculate the percent yield.

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

**Known**

- Actual yield $= 14.9\ g$
- Theoretical yield $= 15.7\ g$

**Unknown**

- Percent yield = ? %

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

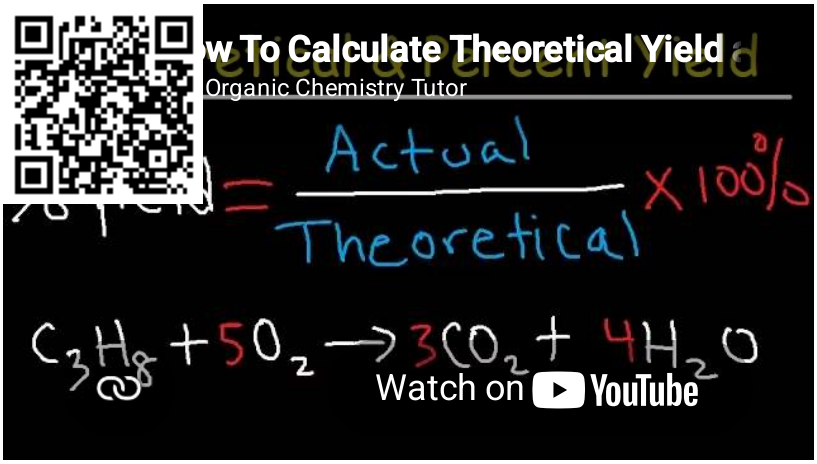
Use the percent yield equation above.

***Step 2: Solve.***

$$\text{Percent Yield} = \frac{14.9\ g}{15.7\ g} \times 100\% = 94.9\%$$

***Step 3: Think about your result.***

Since the actual yield is slightly less than the theoretical yield, the percent yield is just under $100\%$.



## Summary

- Theoretical yield is calculated based on the stoichiometry of the chemical equation.
- The actual yield is experimentally determined.
- The percent yield is determined by calculating the ratio of actual yield/theoretical yield.

## Review

1. What do we need in order to calculate theoretical yield?
2. If I spill some of the product before I weigh it, how will that affect the actual yield?
3. How will spilling some of the product affect the percent yield?
4. I make a product and weigh it before it is dry. How will that affect the actual yield?

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# CHAPTER OVERVIEW

## 17: Gases

Of the three basic phases of matter—solids, liquids, and gases—only one of them has predictable physical properties: gases. In fact, the study of the properties of gases was the beginning of the development of modern chemistry from its alchemical roots. The interesting thing about some of these properties is that they are independent of the identity of the gas. That is, it doesn't matter if the gas is helium gas, oxygen gas, or sulfur vapors; some of their behavior is predictable and, as we will find, very similar. In this chapter, we will review some of the common behaviors of gases.

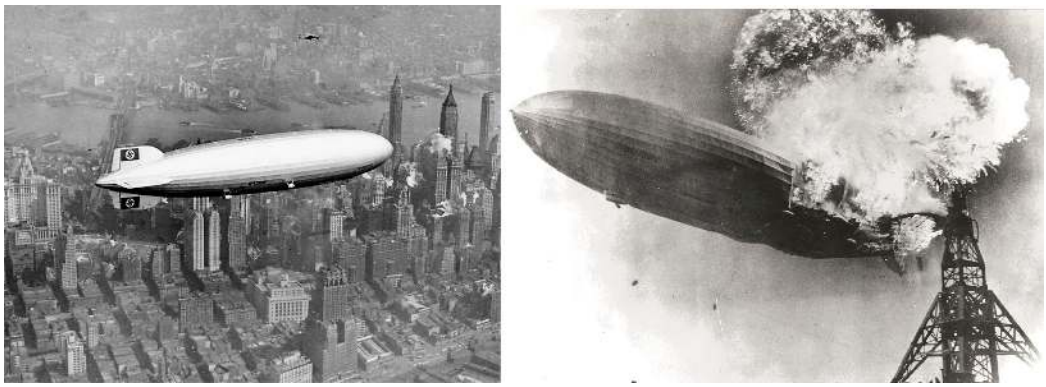
Let us start by reviewing some properties of gases. Gases have no definite shape or volume; they tend to fill whatever container they are in. They can compress and expand, sometimes to a great extent. Gases have extremely low densities, one-thousandth or less the density of a liquid or solid. Combinations of gases tend to mix together spontaneously; that is, they form solutions. Air, for example, is a solution of mostly nitrogen and oxygen. Any understanding of the properties of gases must be able to explain these characteristics.


17.1: Prelude to Gases
17.2: Kinetic Theory of Gases
17.3: Pressure
17.4: Gas Laws
17.5: Other Gas Laws
17.6: Gas Mixtures


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# 17.1: Prelude to Gases

Perhaps one of the most spectacular chemical reactions involving a gas occurred on May 6, 1937, when the German airship *Hindenburg* exploded on approach to the Naval Air Station in Lakehurst, New Jersey. The actual cause of the explosion is still unknown, but the entire volume of hydrogen gas used to float the airship, about 200,000 $m^3$, burned in less than one minute. Thirty-six people, including one on the ground, were killed. Hydrogen is the lightest known gas. Any balloon filled with hydrogen gas will float in air if its mass is not too great. This makes hydrogen an obvious choice for flying machines based on balloons—airships, dirigibles, and blimps.



*The German airship Hindenburg (left) was one of the largest airships ever built. However, it was filled with hydrogen gas and exploded in Lakehurst, New Jersey, at the end of a transatlantic voyage in May 1937 (right).*

However, hydrogen also has one obvious drawback—it burns in air according to the well-known chemical equation:

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

So although hydrogen is an obvious choice, it is also a dangerous choice. Helium gas is also lighter than air and has 92% of the lifting power of hydrogen. Why, then, was helium not used in the *Hindenburg*? In the 1930s, helium was much more expensive. In addition, the best source of helium at the time was the United States, which banned helium exports to pre–World War II Germany. Today all airships use helium, a legacy of the *Hindenburg* disaster.

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# 17.2: Kinetic Theory of Gases

**Learning Objectives**

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**. 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 17.2.1 shows a representation of how we mentally picture the gas phase.

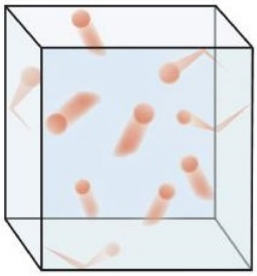


Figure 17.2.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion, with a lot of distance between the particles.

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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# 17.3: Pressure

**Learning Objectives**

- Define *pressure*.
- Learn the units of pressure and how to convert between them.

The kinetic theory of gases indicates that gas particles are always in motion and are colliding with other particles and the walls of the container holding them. Although collisions with container walls are elastic (i.e., there is no net energy gain or loss because of the collision), a gas particle does exert a force on the wall during the collision. The accumulation of all these forces, distributed over the area of the walls of the container, causes pressure. **Pressure** (*P*) is defined as the force of all the gas particle/wall collisions divided by the area of the wall:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

All gases exert pressure; it is one of the fundamental measurable quantities of this phase of matter. Even our atmosphere exerts pressure—in this case, the gas is being "held in" by the earth's gravity, rather than the gas being in a container. The pressure of the atmosphere is about 14.7 pounds of force for every square inch of surface area: 14.7 $\text{lb/in}^2$.

Pressure has a variety of units. The formal, SI-approved unit of pressure is the *pascal* (Pa), which is defined as 1 $\text{N/m}^2$ (one newton of force over an area of one square meter). However, this is usually too small in magnitude to be useful. A common unit of pressure is the **atmosphere** (atm), which was originally defined as the average atmospheric pressure at sea level.

However, "average atmospheric pressure at sea level" is difficult to pinpoint because of atmospheric pressure variations. A more reliable and common unit is **millimeters of mercury** (mmHg), which is the amount of pressure exerted by a column of mercury exactly 1 mm high. An equivalent unit is the **torr**, which equals 1 mmHg. (The torr is named after Evangelista Torricelli, a seventeenth-century Italian scientist who invented the mercury barometer.) With these definitions of pressure, the atmosphere unit is redefined: 1 atm is defined as exactly 760 mmHg, or 760 torr. We thus have the following equivalencies:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr}$$

We can use these equivalencies as with any equivalencies—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

**Example 17.3.1: Pressure Conversion**

How many atmospheres are there in 595 torr?

**Solution**

Using the pressure equivalencies, we construct a conversion factor between torr and atmospheres:

$$\frac{1\,atm}{760\,torr}$$

$$595\ \cancel{torr} \times \frac{1\,atm}{760\ \cancel{torr}} = 0.783\,atm$$

Because the numbers in the conversion factor are exact, the number of significant figures in the final answer is determined by the initial value of pressure.

**Exercise 17.3.1**

How many atmospheres are there in 1,022 torr?

**Answer**

1.345 atm

### Example 17.3.2: Mars

The atmosphere on Mars is largely $CO_2$ at a pressure of 6.01 mmHg. What is this pressure in atmospheres?

**Solution**

Use the pressure equivalencies to construct the proper conversion factor between millimeters of mercury and atmospheres.

$$6.01\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$$

At the end, we expressed the answer in scientific notation.

### Exercise 17.3.2

Atmospheric pressure is low in the eye of a hurricane. In a 1979 hurricane in the Pacific Ocean, a pressure of 0.859 atm was reported inside the eye. What is this pressure in torr?

**Answer**

652 torr

## Summary

- Pressure is a force exerted over an area.
- Pressure has several common units that can be converted.

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# 17.4: Gas Laws

**Learning Objectives**

- Learn what is meant by the term *gas laws*.
- Learn and apply Boyle's law.
- Learn and apply Charles's law.

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure ($P$) and volume ($V$), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [$n$]), if the temperature ($T$) of the gas was kept constant, pressure and volume were related: As one increases, the other decreases. As one decreases, the other increases. 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 for a given amount of gas at a constant temperature:

$$P \times V = \text{constant at constant } n \text{ and } T$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled $P_1$ and $V_1$ and the new conditions are labeled $P_2$ and $V_2$, we have

$$P_1V_1 = \text{constant} = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \text{ at constant } n \text{ and } T$$

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 **17.4.1** shows two representations of how Boyle's law works.

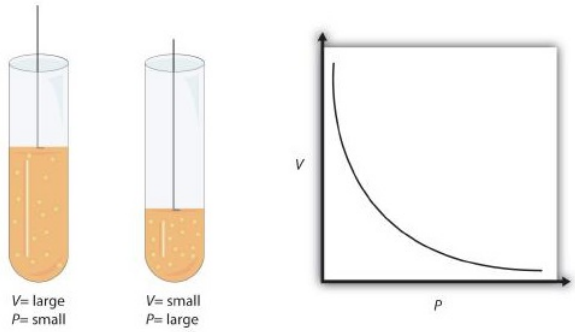



Figure **17.4.1**: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

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 17.4.1

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 17.4.1

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 17.4.2

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 17.4.2**

If $V_1$ = 456 mL, $P_1$ = 308 torr, and $P_2$ = 1.55 atm, what is $V_2$?

**Answer**

119 mL

There are other measurable characteristics of a gas. One of them 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*.

A mathematical relationship between *V* and *T* should be possible except for one thought: what temperature scale should we use? We know from Chapter 2 that science 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:

$$\frac{V}{T} = constant$$

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:

$$K = °C + 273$$

where K represents the temperature in kelvins, and °C represents the temperature in degrees Celsius.

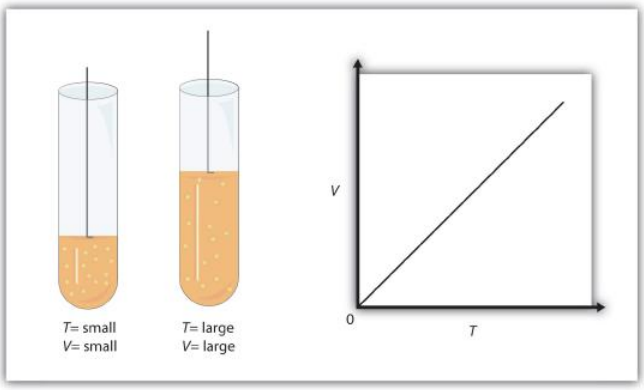



Figure **17.4.2**: Charles's Law. A piston having a certain volume and temperature (left piston) will have twice the volume when its temperature is twice as much (right piston). One can also plot V versus T for a given amount of gas at a certain pressure; such a plot will look like the graph on the right.

## Example 17.4.3

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:

$$\frac{(559\,\cancel{K})(34.8\,ml)}{315\,\cancel{K}} = \frac{V_2(\cancel{559\,K})}{\cancel{559\,K}}$$

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 17.4.3

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 17.4.4

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 17.4.4

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

- 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.
- 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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# 17.5: Other Gas Laws

**Learning Objectives**

- Review other simple gas laws.
- Learn and apply the combined gas law.

You may notice in Boyle's law and Charles's law that we actually refer to four physical properties of a gas: pressure (*P*), volume (*V*), temperature (*T*), and amount (in moles—*n*). We do this because these are the only four independent physical properties of a gas. There are other physical properties, but they are all related to one (or more) of these four properties.

Boyle's law is written in terms of two of these properties, with the other two being held constant. Charles's law is written in terms of two different properties, with the other two being held constant. It may not be surprising to learn that there are other gas laws that relate other pairs of properties—as long as the other two are held constant. In this section, we will mention a few.

**Gay-Lussac's law** relates pressure with absolute temperature. In terms of two sets of data, Gay-Lussac's law is

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

at constant $V$ and $n$.

Note that it has a structure very similar to that of Charles's law, only with different variables—pressure instead of volume. **Avogadro's law** introduces the last variable for amount. The original statement of Avogadro's law states that equal volumes of different gases at the same temperature and pressure contain the same number of particles of gas. Because the number of particles is related to the number of moles (1 mol = $6.022 \times 10^{23}$ 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. Put mathematically into a gas law, Avogadro's law is

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

at constant $V$ and $T$.

(First announced in 1811, it was Avogadro's proposal that volume is related to the number of particles that eventually led to naming the number of things in a mole as Avogadro's number.) Avogadro's law is useful because for the first time we are seeing amount, in terms of the number of moles, as a variable in a gas law.

**Example 17.5.1**

A 2.45 L volume of gas contains $4.5 \times 10^{21}$ gas particles. How many gas particles are there in 3.87 L if the gas is at constant pressure and temperature?

**Solution**

We can set up Avogadro's law as follows:

$$\frac{2.45\ L}{4.5 \times 10^{21}\ \text{particles}} = \frac{3.87\ L}{n_2}$$

We algebraically rearrange to solve for $n_2$:

$$n_2 = \frac{(3.87\ \cancel{L})(4.5 \times 10^{21}\ \text{particles})}{2.45\ \cancel{L}}$$

The L units cancel, so we solve for $n_2$:

$$n_2 = 7.1 \times 10^{21}\ \text{particles}$$

**Exercise 17.5.1**

A 12.8 L volume of gas contains $3.00 \times 10^{20}$ gas particles. At constant temperature and pressure, what volume does $8.22 \times 10^{18}$ gas particles fill?

**Answer**

0.351 L

The variable *n* in Avogadro's law can also stand for the number of moles of gas, in addition to number of particles.

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ at constant } n$$

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.

**Example 17.5.2**

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 17.5.2**

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

As with other gas laws, if you need to determine the value of a variable in the denominator of the combined gas law, you can either cross-multiply all the terms, or just take the reciprocal of the combined gas law. Remember, the variable you are solving for must be in the numerator and all by itself on one side of the equation.

## 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.

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# 17.6: Gas Mixtures

**Learning Objective**

- Learn Dalton's law of partial pressures.

One of the properties of gases is that they mix with each other. When they do so, they become a solution—a homogeneous mixture. Some of the properties of gas mixtures are easy to determine if we know the composition of the gases in the mix.

In gas mixtures, each component in the gas phase can be treated separately. Each component of the mixture shares the same temperature and volume. (Remember that gases expand to fill the volume of their container; gases in a mixture continue to do that as well.) However, each gas has its own pressure. The **partial pressure** of a gas, $P_i$, is the pressure that an individual gas in a mixture has. Partial pressures are expressed in torr, millimeters of mercury, or atmospheres like any other gas pressure; however, we use the term *pressure* when talking about pure gases and the term *partial pressure* when we are talking about the individual gas components in a mixture.

**Dalton's law of partial pressures** states that the total pressure of a gas mixture, $P_{tot}$, is equal to the sum of the partial pressures of the components, $P_i$:

$$P_{tot} = P_1 + P_2 + P_3 + ... = \sum_{\#of\ gases} P_i$$

Although this law may seem trivial, it reinforces the idea that gases behave independently of each other.

**Example 17.6.1:**

A mixture of $H_2$ at 2.33 atm and $N_2$ at 0.77 atm is in a container. What is the total pressure in the container?

**Solution**

Dalton's law of partial pressures states that the total pressure is equal to the sum of the partial pressures. We simply add the two pressures together:

$P_{tot}$ = 2.33 atm + 0.77 atm = 3.10 atm

**Exercise 17.6.1**

$N_2$ and $O_2$. In 760 torr of air, the partial pressure of $N_2$ is 608 torr. What is the partial pressure of $O_2$?

**Answer**

152 torr

**Food and Drink Application: Carbonated Beverages**

Carbonated beverages—sodas, beer, sparkling wines—have one thing in common: they have $CO_2$ gas dissolved in them in such sufficient quantities that it affects the drinking experience. Most people find the drinking experience pleasant—indeed, in the United States alone, over $1.5 \times 10^9$ gal of soda are consumed each year, which is almost 50 gal per person! This figure does not include other types of carbonated beverages, so the total consumption is probably significantly higher.

All carbonated beverages are made in one of two ways. First, the flat beverage is subjected to a high pressure of $CO_2$ gas, which forces the gas into solution. The carbonated beverage is then packaged in a tightly-sealed package (usually a bottle or a can) and sold. When the container is opened, the $CO_2$ pressure is released, resulting in the well-known *hiss* of an opening container, and $CO_2$ bubbles come out of solution. This must be done with care: if the $CO_2$ comes out too violently, a mess can occur!



Figure **17.6.1** Carbonated beverage © Thinkstock. If you are not careful opening a container of a carbonated beverage, you can make a mess, as the $CO_2$ comes out of solution suddenly.

The second way a beverage can become carbonated is by the ingestion of sugar by yeast, which then generates $CO_2$ as a digestion product. This process is called *fermentation*. The overall reaction is

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(aq)$$

When this process occurs in a closed container, the $CO_2$ produced dissolves in the liquid, only to be released from solution when the container is opened. Most fine sparkling wines and champagnes are turned into carbonated beverages this way. Less-expensive sparkling wines are made like sodas and beer, with exposure to high pressures of $CO_2$ gas.

## Summary

- The pressure of a gas in a gas mixture is termed the *partial pressure*.
- Dalton's law of partial pressure says that the total pressure in a gas mixture is the sum of the individual partial pressures.

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# CHAPTER OVERVIEW

## 18: Solutions

Solutions are all around us. Air, for example, is a solution. If you live near a lake, a river, or an ocean, that body of water is not pure $H_2O$ but most probably a solution. Much of what we drink—for example, soda, coffee, tea, and milk—is at least in part a solution. Solutions are a large part of everyday life. A lot of the chemistry occurring around us happens in solution. In fact, much of the chemistry that occurs in our own bodies takes place in solution, and many solutions—such as the Ringer's lactate IV solution—are important for our health. In our understanding of chemistry, we need to understand a little bit about solutions. In this chapter, you will learn about the special characteristics of solutions, how solutions are characterized, and some of their properties.


18.1: Prelude to Solutions
18.2: Solutions
18.3: The Dissolution Process
18.4: Solubility Rules
18.5: Molecular and Ionic Equations
18.6: Net Ionic Equations
18.7: Concentration
18.8: Osmotic Pressure
18.9: Osmosis and Diffusion
18.S: Solutions (Summary)


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# 18.1: Prelude to Solutions

If you watch any of the medical dramas on television, you may have heard a doctor (actually an actor) call for an intravenous solution of “Ringer’s lactate” (or “lactated Ringer’s” or "Ri-Lac"). So what is Ringer’s lactate?

Intravenous (IV) solutions are administered for two main reasons:

1. to introduce necessary substances into the bloodstream, such as ions for proper body function, sugar and other food substances for energy, or drugs to treat a medical condition, and
2. to increase the volume of the bloodstream.

Many people with acute or long-term medical conditions have received some type of an IV solution.

One basic IV solution, called a *normal saline solution*, is simply a dilute solution of NaCl dissolved in water. Normal saline is 9.0 g of NaCl dissolved in each liter of solution. *Ringer’s lactate* is a normal saline solution that also has small amounts of potassium and calcium ions mixed in. In addition, it contains about 2.5 g of lactate ions ($C_3H_5O_3^-$) per liter of solution. The liver metabolizes lactate ions into bicarbonate ($HCO_3^-$) ions, which help maintain the acid-base balance of blood. Many medical problems, such as heart attacks and shock, affect the acid-base balance of blood, and the presence of lactate in the IV solution eases problems caused by this imbalance.

Physicians can select from a range of premade IV solutions, in accordance with a patient’s particular needs. Ringer’s lactate is commonly used when a patient’s blood volume must be increased quickly. Another frequently used IV solution, called D5W, is a 5% solution of dextrose (a form of sugar) in water.

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# 18.2: Solutions

**Learning Objectives**

- To understand what causes solutions to form.

A solution is another name for a homogeneous mixture. A *mixture* as a material composed of two or more substances. In a solution, the combination is so intimate that the different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

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 **18.2.1** lists some common types of solutions, with examples of each.

Table **18.2.1**: Types of Solutions

| Solvent Phase | Solute Phase | Example |
|---|---|---|
| gas | gas | air |
| liquid | gas | carbonated beverages |
| liquid | liquid | ethanol ($C_2H_5OH$) in $H_2O$ (alcoholic beverages) |
| liquid | solid | saltwater |
| solid | gas | $H_2$ gas absorbed by Pd metal |
| solid | liquid | Hg(ℓ) in dental fillings |
| solid | solid | steel alloys |

What causes a solution to form? The simple answer is that the solvent and the solute must have similar intermolecular interactions. When this is the case, the individual particles of solvent and solute can easily mix so intimately that each particle of solute is surrounded by particles of solvent, forming a solution. However, if two substances have very different intermolecular interactions, large amounts of energy are required to force their individual particles to mix intimately, so a solution does not form. Thus two alkanes like *n*-heptane, $C_7H_{16}$, and *n*-hexane, $C_6H_{14}$, are completely miscible in all proportions. The $C_7H_{16}$ and $C_6H_{14}$ molecules are so similar (recall Section 4.6) that there are only negligible differences in intermolecular forces.

For a similar reason, methanol, $CH_3OH$, is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and so there are strong intermolecular attractions within each liquid. However, $CH_3OH$ dipoles can align with $H_2O$ dipoles, and $CH_3OH$ molecules can hydrogen bond to $H_2O$ molecules, and so the attractions among unlike molecules in the solution are similar to those among like molecules in each pure liquid.

This process leads to a simple rule of thumb: *like dissolves like*. Solvents that are very polar will dissolve solutes that are very polar or even ionic. Solvents that are nonpolar will dissolve nonpolar solutes. Thus water, being polar, is a good solvent for ionic

compounds and polar solutes like ethanol ($C_2H_5OH$). However, water does not dissolve nonpolar solutes, such as many oils and greases (Figure 18.2.1).



Figure 18.2.1: A beaker holds water with blue food dye (upper liquid layer) and a much more dense perfluoroheptane (a fluorocarbon) lower liquid layer. The two fluids cannot mix and the dye cannot dissolve in fluorocarbon. A goldfish and a crab have been introduced into the water. The goldfish cannot penetrate the dense fluorocarbon. The crab floats at the liquid boundary with only parts of his legs penetrating the fluorocarbon fluid, unable to sink to the bottom of the beaker. Quarter coins rest on the bottom of the beaker. Animals were rescued from their predicament after the photo was taken. Figure used with permission from Wikipedia (Sbharris (Steven B. Harris)).

We use the word soluble to describe a solute that dissolves in a particular solvent, and the word insoluble for a solute that does not dissolve in a solvent. Thus, we say that sodium chloride is soluble in water but insoluble in hexane ($C_6H_{14}$). If the solute and the solvent are both liquids and soluble in any proportion, we use the word miscible, and the word immiscible if they are not.

### ✔ Example 18.2.1

Water is considered a polar solvent. Which substances should dissolve in water?

1. methanol ($CH_3OH$)
2. sodium sulfate ($Na_2SO_4$)
3. octane ($C_8H_{18}$)

#### Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

### ? Exercise 18.2.1

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water ($H_2O$)
b. sodium sulfate ($Na_2SO_4$)
c. octane ($C_8H_{18}$)

#### Answer

Octane only.

### Example 18.2.2

Predict which of the following compounds will be most soluble in water:

a. $\underset{\text{Ethanol}}{CH_3CH_2OH}$

b. $\underset{\text{Hexanol}}{CH_3CH_2CH_2CH_2CH_2CH_2OH}$

#### Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

### 18.2.2 Exercise

Would $I_2$ be more soluble in $CCl_4$ or $H_2O$?

**Answer**

$I_2$ is nonpolar. Of the two solvents, $CCl_4$ is nonpolar and $H_2O$ is polar, so $I_2$ would be expected to be more soluble in $CCl_4$.

## Key Takeaway

- Solutions form because a solute and a solvent experience similar intermolecular interactions.

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# 18.3: The Dissolution Process

**Learning Objectives**

- To describe the dissolution process at the molecular level

## The Dissolution Process

What occurs at the molecular level to cause a solute to dissolve in a solvent? The answer depends in part on the solute, but there are some similarities common to all solutes.

Recall the rule that *like dissolves like*. This means that substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. 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, surrounded by solvent molecules, enter the solution. (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 **18.3.1**. When the solvent is water, the word **hydration**, rather than solvation, is used.

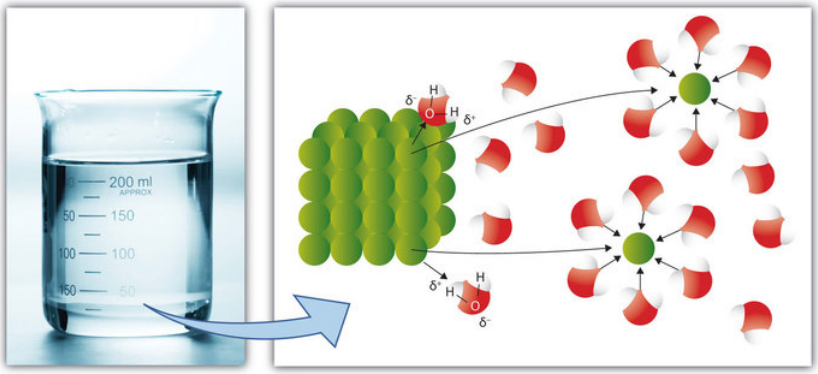



Figure **18.3.1**: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

## 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. That is, the cations and anions of an ionic solute separate when the solute dissolves. This process is referred to as **dissociation** (Figure **18.3.1**).

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 18.3.1**

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 18.3.1**

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.

## Key Takeaway

- When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

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# 18.4: Solubility Rules

To determine if a salt is soluble or to judge whether double-replacement reactions will occur, we need to know what kinds of ionic compounds will be insoluble in aqueous solutions. 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 **18.4.1** 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 **18.4.1**: Some Useful Solubility Rules (soluble)

| These compounds generally dissolve in water (are soluble): | Exceptions: |
|---|---|
| All compounds of $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, and $NH_4^+$ | None |
| All compounds of $NO_3^-$ and $C_2H_3O_2^-$ | 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 **18.4.2**: Some Useful Solubility Rules (insoluble)

| 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:

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

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure **18.4.2**).




Figure **18.4.2**: 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, http://commons.wikimedia.org/wiki/File:Copper_solution.jpg.

**Example 18.4.4:**

Will a double-replacement 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

$$\mathrm{2\,NaOH\,(aq) + FeCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + Fe(OH)_2\,(s)}$$

**Exercise 18.4.4**

$$\mathrm{Sr(NO_3)_2 + KCl \longrightarrow}$$

**Answer**

No reaction; all possible products are soluble.

## Key Takeaways

- Solubility rules are used to predict whether some double-replacement reactions will occur.

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# 18.5: Molecular and Ionic Equations

One of the unfortunate byproducts of industrialized society is acid rain. Sulfur dioxide from burning coal and nitrogen oxides from vehicle emissions both form acids. When these acids react with limestone (calcium carbonate), reactions occur that dissolve the limestone and release water and carbon dioxide. Over a period of time, serious damage is caused to the limestone structure.

## Molecular and Ionic Equations

When ionic compounds are dissolved into water, the polar water molecules break apart the solid crystal lattice, resulting in the hydrated ions being evenly distributed through the water. This process is called dissociation and is the reason that all ionic compounds are strong electrolytes. When two different ionic compounds that have been dissolved in water are mixed, a chemical reaction may occur between certain pairs of the hydrated ions. Consider the double-replacement reaction that occurs when a solution of sodium chloride is mixed with a solution of silver nitrate:

$$\mathrm{NaCl}\,(aq) + \mathrm{AgNO_3}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s)$$

The driving force behind this reaction is the formation of the silver chloride precipitate (see figure below).

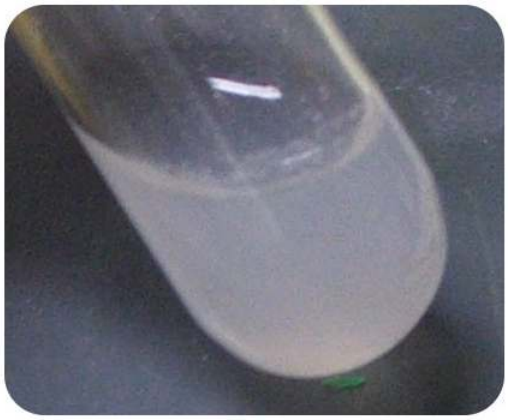


Figure 18.5.1: The white silver chloride precipitate instantly forms when a solution of silver nitrate is added to a solution of sodium chloride.

This is called a molecular equation. A **molecular equation** is an equation in which the formulas of the compounds are written as though all substances exist as molecules. However, there is a better way to show what is happening in this reaction. All of the aqueous compounds should be written as ions, because they are present in the water as separated ions—a result of their dissociation.

$$\mathrm{Na^+}\,(aq) + \mathrm{Cl^-}\,(aq) + \mathrm{Ag^+}\,(aq) + \mathrm{NO_3^-}\,(aq) \rightarrow \mathrm{Na^+}\,(aq) + \mathrm{NO_3^-}\,(aq) + \mathrm{AgCl}\,(s)$$

This equation is called an **ionic equation**, an equation in which dissolved ionic compounds are shown as free ions.

Some other double-replacement reactions do not produce a precipitate as one of the products. The production of a gas and/or a molecular compound such as water may also drive the reaction. For example, consider the reaction of a solution of sodium carbonate with a solution of hydrochloric acid ($\mathrm{HCl}$). The products of the reaction are aqueous sodium chloride, carbon dioxide, and water. The balanced molecular equation is:

$$\mathrm{Na_2CO_3}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

The ionic equation is:

$$2\mathrm{Na^+}\,(aq) + \mathrm{CO_3^{2-}}\,(aq) + 2\mathrm{H^+}\,(aq) + 2\mathrm{Cl^-}\,(aq) \rightarrow 2\mathrm{Na^+}\,(aq) + 2\mathrm{Cl^-}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

A single-replacement reaction is one in which an element replaces another element in a compound. An element is in either the solid, liquid, or gas state and is not an ion. The example below shows the reaction of solid magnesium metal with aqueous silver nitrate to form aqueous magnesium nitrate and silver metal.

Balanced molecular equation:

$$\mathrm{Mg}\,(s) + 2\mathrm{AgNO_3}\,(aq) \rightarrow \mathrm{Mg(NO_3)_2}\,(aq) + 2\mathrm{Ag}\,(s)$$

Ionic equation:

$$\mathrm{Mg}\,(s) + 2\mathrm{Ag^+}\,(aq) + 2\mathrm{NO_3^-}\,(aq) \rightarrow \mathrm{Mg^{2+}}\,(aq) + 2\mathrm{NO_3^-}\,(aq) + \mathrm{Ag}\,(s)$$

This type of single-replacement reaction is called a metal replacement. Other common categories of single-replacement reactions are: hydrogen replacement and halogen replacement.

## Summary

- A molecular equation is an equation in which the formulas of the compounds are written as though all substances exist as molecules.
- An ionic equation is one in which dissolved ionic compounds are shown as free ions.
- Examples of molecular and ionic equations are shown.

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# 18.6: Net Ionic Equations

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:

$$\mathrm{Na^+}\,(aq) + \mathrm{Cl^-}\,(aq) + \mathrm{Ag^+}\,(aq) + \mathrm{NO_3^-}\,(aq) \rightarrow \mathrm{Na^+}\,(aq) + \mathrm{NO_3^-}\,(aq) + \mathrm{AgCl}\,(s)$$

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.

Example 18.6.1

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:

$$3\mathrm{Cu^{2+}}\,(aq) + 6\mathrm{Cl^-}\,(aq) + 6\mathrm{K^+}\,(aq) + 2\mathrm{PO_4^{3-}}\,(aq) \rightarrow 6\mathrm{K^+}\,(aq) + 6\mathrm{Cl^-}\,(aq) + \mathrm{Cu_3(PO_4)_2}\,(s)$$

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, $\mathrm{K^+}$ and $\mathrm{Cl^-}$, can be eliminated.

Net ionic equation:

$$\mathrm{3Cu^{2+}}\,(aq) + \mathrm{2PO_4^{3-}}\,(aq) \rightarrow \mathrm{Cu_3(PO_4)_2}\,(s)$$

***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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# 18.7: Concentration

**Learning Objectives**

- Calculate percentage concentration (m/m, v/v, m/v), ppm and ppb.
- Calculate the molarity of a solution.
- Use concentration units to calculate the amount of solute in a solution.
- Use molarity to determine quantities in chemical reactions.
- Determine the resulting concentration of a diluted solution.

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 **18.7.1** lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table **18.7.1** includes the temperature at which the solubility was determined.

Table **18.7.1**: Solubilities of Various Solutes in Water at 25°C (Except as Noted)

| Substance | Solubility (g in 100 mL of H2O) |
|---|---|
| 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 **18.7.1**. 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.

### Precipitation from Supersaturated Solutions

Recrystallization of excess solute from a supersaturated solution usually gives off energy as heat. Commercial heat packs containing supersaturated sodium acetate ($NaC_2H_3O_2$) take advantage of this phenomenon. You can probably find them at your local drugstore.




***Video* 18.7.1*:*** Watered-down sodium acetate trihydrate. Needle crystal is truly wonderful structures

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.

## Percent Composition

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:

$$\%\,\mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \tag{18.7.1}$$

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 18.7.1

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 18.7.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of $2.00 \times 10^2$ g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

**Answer**

7.90%

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:

$$\%\ \text{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \tag{18.7.2}$$

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 18.7.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\%\ \text{m/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\% \tag{18.7.3}$$



Figure 18.7.1: 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 Composition 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 solution of alcohol**, this means that there are 5 mL of alcohol dissolved in every 100 mL solution.

**5 mL alcohol = 100 mL solution**

The two possible conversion factors are written as follows:

$$\frac{\text{5 mL alcohol}}{\text{100 mL solution}} \text{ or } \frac{\text{100 mL solution}}{\text{5 mL alcohol}}$$

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 18.7.2**

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 18.7.2**

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 18.7.3**

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 L = 1,000 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 18.7.3**

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**

$$\%\ \text{m/v} = \frac{27.0\ \text{g NaOCl}}{500.0\ \text{mL solution}} \times 100\% = 5.40\%\ \text{m/v}$$

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:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000 \tag{18.7.4}$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000,000 \tag{18.7.5}$$

> *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 18.7.4**

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 18.7.4**

An 85 kg body contains 0.012 g of Ni. What is the concentration of Ni in parts per million?

**Answer**

0.14 ppm

## 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 is defined as the number of moles of a solute dissolved per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{18.7.6}$$

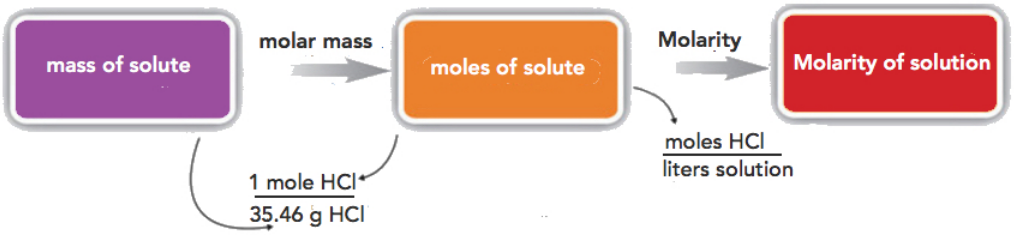
Molarity is abbreviated M (often referred to as "molar"), and the units are often abbreviated as mol/L. It is important to remember that "mol" in this expression refers to moles of solute and that "L" refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl} \tag{18.7.7}$$

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):**

$$22.4\,\cancel{gHCl} \times \frac{1\,mol\,HCl}{36.46\,\cancel{gHCl}} = 0.614\,mol\,HCl \tag{18.7.8}$$

Step 2: use the **definition of molarity** to determine the concentration:

$$M = \frac{0.614\,mol\,HCl}{1.56L\,solution} = 0.394\,MHCl \tag{18.7.9}$$

**Example 18.7.5**

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 18.7.5**

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**.

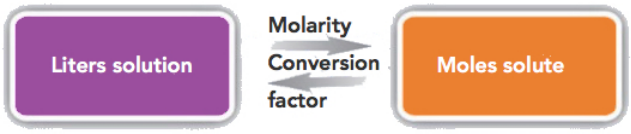
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a **3.0 M solution of sucrose** means that there are three moles of sucrose dissolved in every **liter of solution**. Mathematically, this is stated as follows:

**3.0 moles sucrose = 1 L solution**

Dividing both sides of this expression by either side, we generate two possible conversion factors:

$$\frac{3.0\ \text{mol sucrose}}{1\ \text{L solution}} \text{ or } \frac{1\ \text{L solution}}{3.0\ \text{mol sucrose}}$$

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.

$$0.108\ \cancel{L\ solution} \times \frac{3.0\ mol\ sucrose}{\cancel{1\ L\ solution}} = 0.32\ mol\ sucrose \tag{18.7.10}$$

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.

$$4.88\ \cancel{mol\ sucrose} \times \frac{1\ L\ solution}{\cancel{3.0\ mol\ sucrose}} = 1.63\ L\ solution \tag{18.7.11}$$

**Example 18.7.6**

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.

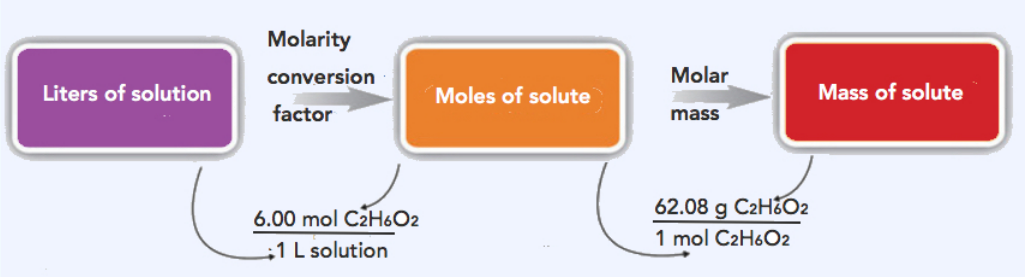
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} = 30.0\ \text{mol}\ C_2H_6O_2$$

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.

**Example 18.7.6A**

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**

This is an alternative method in case you don't want to use the conversion factor for molarity. In both parts, we will use the definition of molarity to solve for the desired quantity.

1. $$0.0753\ \text{M} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{\text{volume of solution}}$$

   To solve for the volume of solution, we multiply both sides by volume of solution and divide both sides by the molarity value to isolate the volume of solution on one side of the equation:

   $$\text{volume of solution} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{0.0753\ \text{M}} = 5.98\ \text{L}$$

   Note that because the definition of molarity is mol/L, the division of mol by M yields L, a unit of volume.

2. The molar mass of $C_2H_6O_2$ is 62.08 g/mol., so

   $$6.00\ \text{M} = \frac{\text{moles of solute}}{5.00\ \text{L}}$$

   To solve for the number of moles of solute, we multiply both sides by the volume:

   $$\text{moles of solute} = (6.00\ \text{M})(5.00\ \text{L}) = 30.0\ \text{mol}$$

   Note that because the definition of molarity is mol/L, the product M × L gives mol, a unit of amount. Now, using the molar mass of $C_3H_8O_3$, we convert mol to g:

   $$30.0\ \text{mol} \times \frac{62.08\ \text{g}}{\text{mol}} = 1,860\ \text{g}$$

   Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

**Exercise 18.7.6**

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

## Using Molarity in Stoichiometry Problems

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:

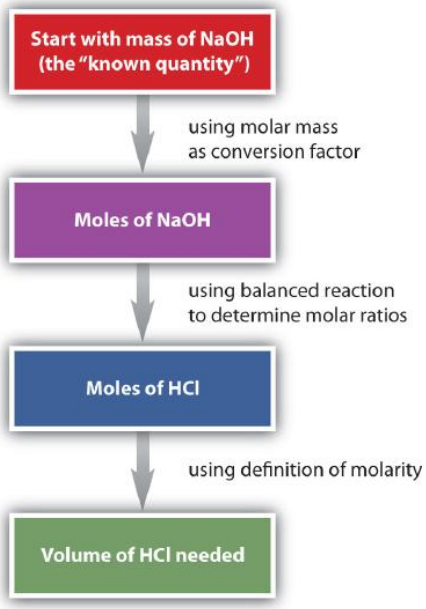



***Figure* 18.7.2**: *Typical approach to solving Molarity problems*

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 18.7.7**

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:

$$4.63\ \text{mol NaOH} \times \frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}} = 4.63\ \text{mol HCl}$$

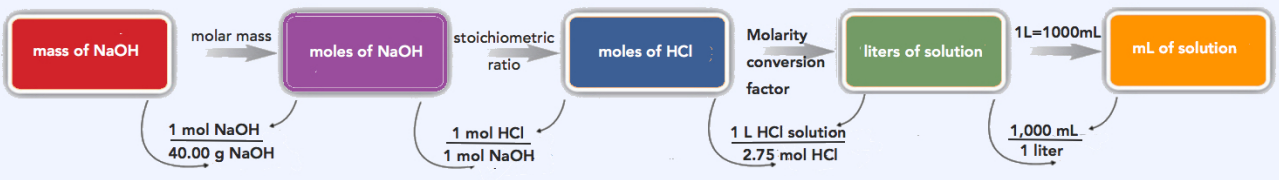
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$2.75\ \text{M HCl} = \frac{4.63\ \text{mol HCl}}{\text{volume of HCl solution}}$$

$$\text{volume of HCl} = \frac{4.63\ \text{mol HCl}}{2.75\ \text{M HCl}} = 1.68\ \text{L} \times \frac{1,000\ \text{mL}}{1\ \text{L}} = 1,680\ \text{mL}$$

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 18.7.7**

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 general steps for performing stoichiometry problems such as this are shown in Figure **18.7.3**. You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure **18.7.3** 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.

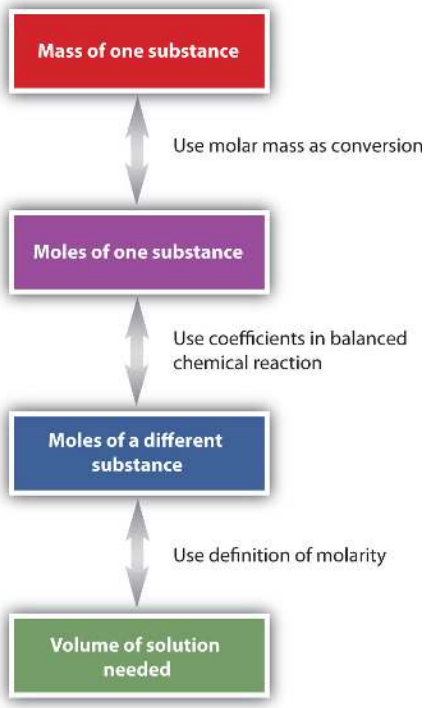



Figure **18.7.3**: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table **18.7.2** lists the typical concentrations of some of these solutes.

Table **18.7.2**: 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!

## 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. (For more information about the ions present in blood plasma, see Chapter 3 "Ionic Bonding and Simple Ionic Compounds", Section 3.3 "Formulas for Ionic Compounds".)

**Exercise 18.7.8*a***

a) How many equivalents (Eq) would 1 mole of $Al^{3+}$ equal?

b) How many equivalents (Eq) would 2 mole of $Cl^-$ equal?

c) How many equivalents (Eq) would 3.5 mole of $CO_3^{2-}$ equal?

**Answer**

a. 3 Eq

b. 2 Eq

c. 7 Eq

## Dilutions

When additional water is added to an aqueous solution, the concentration of that solution decreases. This is because the number of **moles of the solute does not change**, while the **volume of the solution increases**. We can set up an equality between the moles of the solute before the dilution (1) and the moles of the solute after the dilution (2).

$$\text{mol}_1 = \text{mol}_2 \tag{18.7.12}$$

Since the moles of solute in a solution is equal to the molarity multiplied by the liters, we can set those equal.

$$M_1 \times L_1 = M_2 \times L_2 \tag{18.7.13}$$

Finally, because the two sides of the equation are set equal to one another, the volume can be in any units we choose, as long as that unit is the same on both sides. Our equation for calculating the molarity of a diluted solution becomes:

$$M_1 \times V_1 = M_2 \times V_2 \tag{18.7.14}$$

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of $\text{HCl}$. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for $M_2$.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl} \tag{18.7.15}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

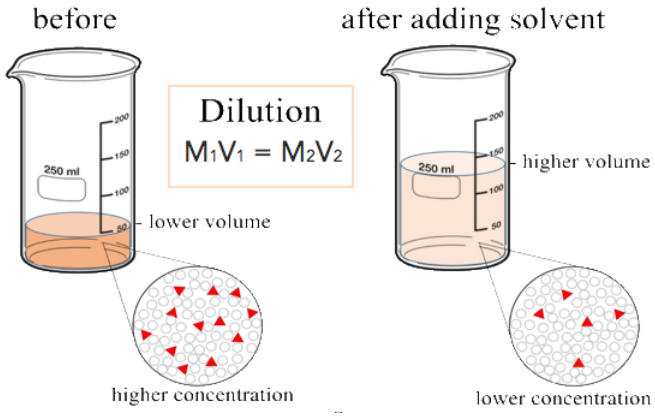



Figure 18.7.1: Figure 18.7.4: Diluting a solution by adding more solvent. Through the dilution process, the volume increases and the concentrations of the solutes decrease. As a consequence, there is more solution in the beaker after dilution, and the color of the solution becomes fainter. The inset shows that at the particular level (picometer to nanometer scale), there are less solute particles (red triangles) per volume. The content in the central box shows the dilution law, i.e. that the product of concentration and volume stays constant upon dilution. CC BY-SA 4.0.

## Dilution Equations

Any units of concentration and volume can be used, as long as both concentrations and both volumes have the same unit. For example, if we are using M (molarity), then we can express the equation as follows:

$$\text{Molarity}_{\text{initial}} \times \text{volume}_{\text{initial}} = \text{Molarity}_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$M_1V_1 = M_2V_2$$

If we are using percent, the dilution equation is as follows:

$$\%_{initial} \times volume_{initial} = \%_{final} \times volume_{final} \text{ or}$$

$$\%_1V_1 = \%_2V_2$$

## Example 18.7.8

A 125 mL sample of 0.900 M NaCl is diluted to 1,125 mL. What is the final concentration of the diluted solution?

**Solution**

Because the volume units are the same, and we are looking for the molarity of the final solution, we can use (concentration × volume)$_{initial}$ = (concentration × volume)$_{final}$:

$$(0.900\ M \times 125\ mL) = (\text{concentration} \times 1{,}125\ mL)$$

We solve by isolating the unknown concentration by itself on one side of the equation. Dividing by 1,125 mL gives

$$\text{concentration} = \frac{0.900\ M \times 125\ mL}{1{,}125\ mL} = 0.100\ M$$

as the final concentration.

## Exercise 18.7.8

a. A nurse uses a syringe to inject 5.00 mL of 0.550 M heparin solution (heparin is an anticoagulant drug) into a 250 mL IV bag, for a final volume of 255 mL. What is the concentration of the resulting heparin solution?

b. 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**

a. 0.0108 M

b. 135.4 mL

## 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 18.7.5:*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 an easy calculation to determine 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!

## Key Takeaways

- Various concentration units are used to express the amounts of solute in a solution.
- Concentration units can be used as conversion factors in stoichiometry problems.
- New concentrations can be easily calculated if a solution is diluted.

## Concept Review Exercises

1. What are some of the units used to express concentration?
2. Distinguish between the terms *solubility* and *concentration*.

## Answers

1. % m/m, % m/v, ppm, ppb, molarity, and Eq/L (answers will vary)
2. Solubility is typically a limit to how much solute can dissolve in a given amount of solvent. Concentration is the quantitative amount of solute dissolved at any concentration in a solvent.

## Exercises

1. Define *solubility*. Do all solutes have the same solubility?
2. Explain why the terms *dilute* or *concentrated* are of limited usefulness in describing the concentration of solutions.
3. If the solubility of sodium chloride (NaCl) is 30.6 g/100 mL of $H_2O$ at a given temperature, how many grams of NaCl can be dissolved in 250.0 mL of $H_2O$?
4. If the solubility of glucose ($C_6H_{12}O_6$) is 120.3 g/100 mL of $H_2O$ at a given temperature, how many grams of $C_6H_{12}O_6$ can be dissolved in 75.0 mL of $H_2O$?
5. How many grams of sodium bicarbonate ($NaHCO_3$) can a 25.0°C saturated solution have if 150.0 mL of $H_2O$ is used as the solvent?
6. If 75.0 g of potassium bromide (KBr) are dissolved in 125 mL of $H_2O$, is the solution saturated, unsaturated, or supersaturated?
7. Calculate the mass/mass percent of a saturated solution of NaCl. Use the data from Table **18.7.1** "Solubilities of Various Solutes in Water at 25°C (Except as Noted)", assume that masses of the solute and the solvent are additive, and use the density of $H_2O$ (1.00 g/mL) as a conversion factor.
8. Calculate the mass/mass percent of a saturated solution of $MgCO_3$ Use the data from Table **18.7.1** "Solubilities of Various Solutes in Water at 25°C (Except as Noted)", assume that masses of the solute and the solvent are additive, and use the density of $H_2O$ (1.00 g/mL) as a conversion factor.
9. Only 0.203 mL of $C_6H_6$ will dissolve in 100.000 mL of $H_2O$. Assuming that the volumes are additive, find the volume/volume percent of a saturated solution of benzene in water.
10. Only 35 mL of aniline ($C_6H_5NH_2$) will dissolve in 1,000 mL of $H_2O$. Assuming that the volumes are additive, find the volume/volume percent of a saturated solution of aniline in water.
11. A solution of ethyl alcohol ($C_2H_5OH$) in water has a concentration of 20.56% v/v. What volume of $C_2H_5OH$ is present in 255 mL of solution?
12. What mass of KCl is present in 475 mL of a 1.09% m/v aqueous solution?
13. The average human body contains 5,830 g of blood. What mass of arsenic is present in the body if the amount in blood is 0.55 ppm?
14. The Occupational Safety and Health Administration has set a limit of 200 ppm as the maximum safe exposure level for carbon monoxide (CO). If an average breath has a mass of 1.286 g, what is the maximum mass of CO that can be inhaled at that maximum safe exposure level?
15. Which concentration is greater—15 ppm or 1,500 ppb?
16. Express the concentration 7,580 ppm in parts per billion.
17. What is the molarity of 0.500 L of a potassium chromate solution containing 0.0650 mol of $K_2CrO_4$?
18. What is the molarity of 4.50 L of a solution containing 0.206 mol of urea [$(NH_2)_2CO$]?
19. What is the molarity of a 2.66 L aqueous solution containing 56.9 g of NaBr?
20. If 3.08 g of $Ca(OH)_2$ is dissolved in enough water to make 0.875 L of solution, what is the molarity of the $Ca(OH)_2$?
21. What mass of HCl is present in 825 mL of a 1.25 M solution?
22. What mass of isopropyl alcohol ($C_3H_8O$) is dissolved in 2.050 L of a 4.45 M aqueous $C_3H_8O$ solution?
23. What volume of 0.345 M NaCl solution is needed to obtain 10.0 g of NaCl?
24. How many milliliters of a 0.0015 M cocaine hydrochloride ($C_{17}H_{22}ClNO_4$) solution is needed to obtain 0.010 g of the solute?
25. Aqueous calcium chloride reacts with aqueous silver nitrate according to the following balanced chemical equation:

$$CaCl_2(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$$

How many moles of AgCl(s) are made if 0.557 L of 0.235 M $CaCl_2$ react with excess $AgNO_3$? How many grams of AgCl are made?

26. Sodium bicarbonate ($NaHCO_3$) is used to react with acid spills. The reaction with sulfuric acid ($H_2SO_4$) is as follows:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(\ell) + 2CO_2(g)$$

If 27.6 mL of a 6.25 M $H_2SO_4$ solution were spilled, how many moles of $NaHCO_3$ would be needed to react with the acid? How many grams of $NaHCO_3$ is this?

27. The fermentation of glucose to make ethanol and carbon dioxide has the following overall chemical equation:

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

If 1.00 L of a 0.567 M solution of $C_6H_{12}O_6$ were completely fermented, what would be the resulting concentration of the $C_2H_5OH$ solution? How many moles of $CO_2$ would be formed? How many grams is this? If each mole of $CO_2$ had a volume of 24.5 L, what volume of $CO_2$ is produced?

28. Aqueous sodium bisulfite gives off sulfur dioxide gas when heated:

$$2NaHSO_3(aq) \rightarrow Na_2SO_3(aq) + H_2O(\ell) + SO_2(g)$$

If 567 mL of a 1.005 M $NaHSO_3$ solution were heated until all the $NaHSO_3$ had reacted, what would be the resulting concentration of the $Na_2SO_3$ solution? How many moles of $SO_2$ would be formed? How many grams of $SO_2$ would be formed? If each mole of $SO_2$ had a volume of 25.78 L, what volume of $SO_2$ would be produced?

29. What is the concentration of a 1.0 M solution of $K^+(aq)$ ions in equivalents/liter?

30. What is the concentration of a 1.0 M solution of $SO_4^{2-}(aq)$ ions in equivalents/liter?

31. A solution having initial concentration of 0.445 M and initial volume of 45.0 mL is diluted to 100.0 mL. What is its final concentration?

32. A 50.0 mL sample of saltwater that is 3.0% m/v is diluted to 950 mL. What is its final mass/volume percent?

## Answers

1. Solubility is the amount of a solute that can dissolve in a given amount of solute, typically 100 mL. The solubility of solutes varies widely.

2. The term *dilute* means relatively less solute and the term *concentrated* implies relatively more solute. Both are of limited usefulness because these are not accurate.

3. 76.5 g

4. 90.2 g

5. 12.6 g

6. unsaturated

7. 26.5%

8. 2.15%

9. 0.203%

10. 3.4%

11. 52.4 mL
12. 5.18 g
13. 0.00321 g
14. $2.57 \times 10^{-4}$ g
15. 15 ppm
16. 7,580,000 ppb
17. 0.130 M
18. 0.0458 M
19. 0.208 M
20. 0.0475 M
21. 37.6 g
22. 548 g
23. 0.496 L
24. 20 mL
25. 0.262 mol; 37.5 g
26. 0.345 mol; 29.0 g
27. 1.13 M $C_2H_5OH$; 1.13 mol of $CO_2$; 49.7 g of $CO_2$; 27.7 L of $CO_2$
28. 0.503 M $Na_2SO_3$; 0.285 mol $SO_2$; 18.3 g $SO_2$; 471 L $SO_2$
29. 1.0 Eq/L
30. 2.0 Eq/L
31. 0.200 M
32. 0.16 % m/v

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# 18.8: Osmotic Pressure

**Learning Objectives**

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 18.8.1, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

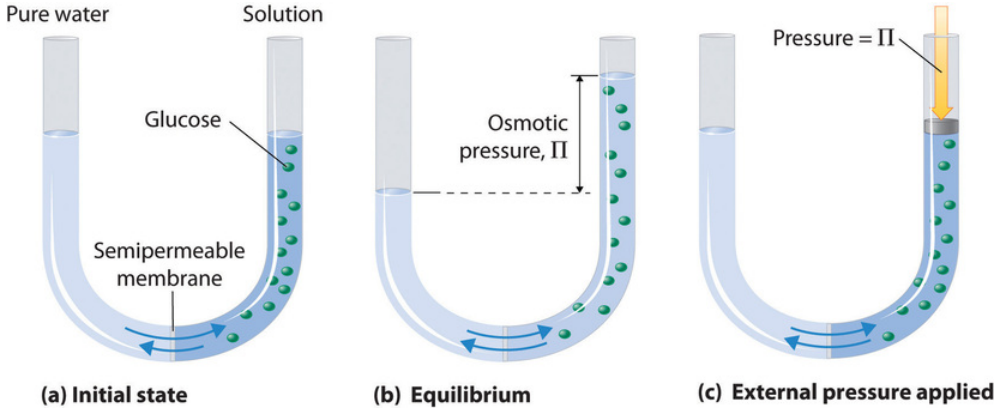



Figure 18.8.1: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution ( $\Pi_{soln}$), *equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.*

The osmotic pressure of a solution depends on the concentration of dissolved solute particles. where

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 18.8.2, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

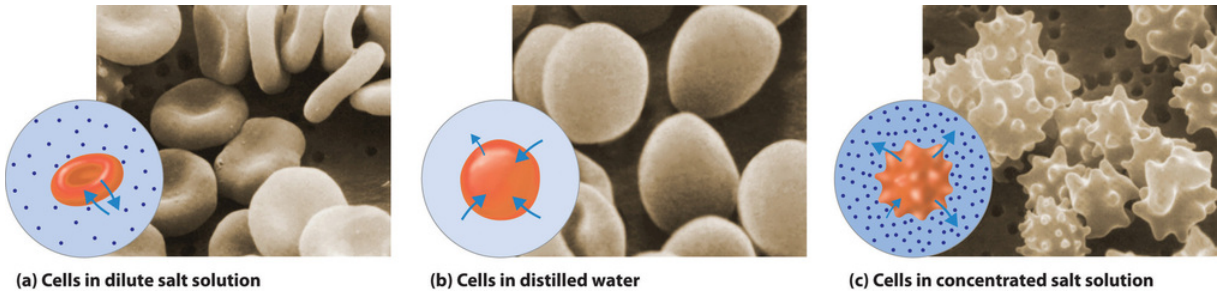



Figure **18.8.2**: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function.

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure **18.8.3**, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

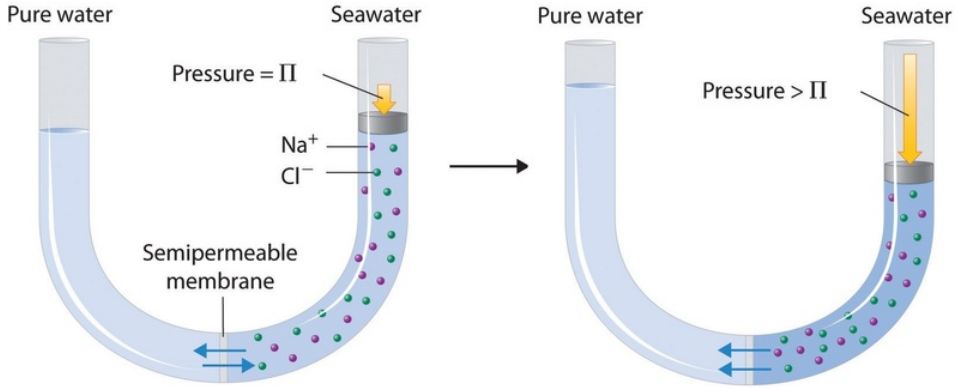



Figure **18.8.3**: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure ($\Pi_{soln}$), *there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely.*

## Summary

When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through.

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# 18.9: Osmosis and Diffusion

**Learning Outcomes**

- Define osmosis and diffusion.
- Distinguish among hypotonic, hypertonic, and isotonic solutions.
- Describe a semipermeable membrane.
- Predict behavior of blood cells in different solution types.
- Describe flow of solvent molecules across a membrane.
- Identify the polar and nonpolar regions of a cell membrane.
- Explain the components present in a phospholipid.

Fish cells, like all cells, have semipermeable membranes. Eventually, the concentration of "stuff" on either side of them will even out. A fish that lives in salt water will have somewhat salty water inside itself. Put it in freshwater, and the freshwater will, through osmosis, enter the fish, causing its cells to swell, and the fish will die. What will happen to a freshwater fish in the ocean?

## Osmosis

Imagine you have a cup that has $100\ \text{mL}$ water, and you add $15\ \text{g}$ of table sugar to the water. The sugar dissolves and the mixture that is now in the cup is made up of a **solute** (the sugar) that is dissolved in the **solvent** (the water). The mixture of a solute in a solvent is called a **solution**.

Imagine now that you have a second cup with $100\ \text{mL}$ of water, and you add $45\ \text{g}$ of table sugar to the water. Just like the first cup, the sugar is the solute, and the water is the solvent. But now you have two mixtures of different solute concentrations. In comparing two solutions of unequal solute concentration, the solution with the higher solute concentration is **hypertonic**, and the solution with the lower solute concentration is **hypotonic**. Solutions of equal solute concentration are **isotonic**. The first sugar solution is hypotonic to the second solution. The second sugar solution is hypertonic to the first.

You now add the two solutions to a beaker that has been divided by a semipermeable membrane, with pores that are too small for the sugar molecules to pass through, but are big enough for the water molecules to pass through. The hypertonic solution is one side of the membrane and the hypotonic solution on the other. The hypertonic solution has a lower water concentration than the hypotonic solution, so a concentration gradient of water now exists across the membrane. Water molecules will move from the side of higher water concentration to the side of lower concentration until both solutions are isotonic. At this point, **equilibrium** is reached.

Red blood cells behave the same way (see figure below). When red blood cells are in a hypertonic (higher concentration) solution, water flows out of the cell faster than it comes in. This results in *crenation* (shriveling) of the blood cell. On the other extreme, a red blood cell that is hypotonic (lower concentration outside the cell) will result in more water flowing into the cell than out. This results in swelling of the cell and potential *hemolysis* (bursting) of the cell. In an isotonic solution, the flow of water in and out of the cell is happening at the same rate.

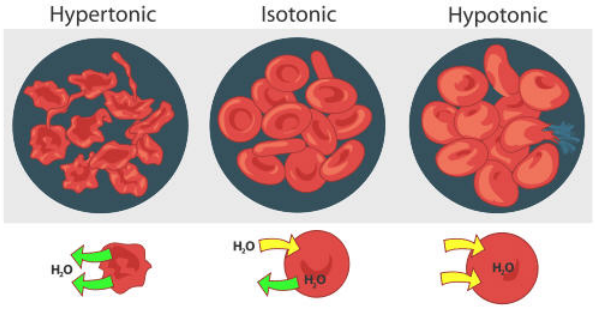



Figure 9.7.1: Red blood cells in hypertonic, isotonic, and hypotonic solutions.

**Osmosis** is the diffusion of water molecules across a semipermeable membrane from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water). Water moves into and

out of cells by osmosis.

- If a cell is in a hypertonic solution, the solution has a lower water concentration than the cell cytosol, and water moves out of the cell until both solutions are isotonic.
- Cells placed in a hypotonic solution will take in water across their membranes until both the external solution and the cytosol are isotonic.

A red blood cell will swell and undergo hemolysis (burst) when placed in a hypotonic solution. When placed in a hypertonic solution, a red blood cell will lose water and undergo *crenation* (shrivel). Animal cells tend to do best in an isotonic environment, where the flow of water in and out of the cell is occurring at equal rates.

## Diffusion

**Passive transport** is a way that small molecules or ions move across the cell membrane without input of energy by the cell. The three main kinds of passive transport are diffusion (or simple diffusion), osmosis, and facilitated diffusion. Simple diffusion and osmosis do not involve transport proteins. Facilitated diffusion requires the assistance of proteins.

**Diffusion** is the movement of molecules from an area of high concentration of the molecules to an area with a lower concentration. For cell transport, diffusion is the movement of small molecules across the cell membrane. The difference in the concentrations of the molecules in the two areas is called the **concentration gradient**. The kinetic energy of the molecules results in random motion, causing diffusion. In simple diffusion, this process proceeds without the aid of a transport protein. It is the random motion of the molecules that causes them to move from an area of high concentration to an area with a lower concentration.

Diffusion will continue until the concentration gradient has been eliminated. Since diffusion moves materials from an area of higher concentration to the lower, it is described as moving solutes "down the concentration gradient". The end result is an equal concentration, or **equilibrium**, of molecules on both sides of the membrane. At equilibrium, movement of molecules does not stop. At equilibrium, there is equal movement of materials in both directions.

Not everything can make it into your cells. Your cells have a plasma membrane that helps to guard your cells from unwanted intruders.

## The Plasma Membrane and Cytosol

If the outside environment of a cell is water-based, and the inside of the cell is also mostly water, something has to make sure the cell stays intact in this environment. What would happen if a cell dissolved in water, like sugar does? Obviously, the cell could not survive in such an environment. So something must protect the cell and allow it to survive in its water-based environment. All cells have a barrier around them that separates them from the environment and from other cells. This barrier is called the **plasma membrane**, or cell membrane.

### The Plasma Membrane

The plasma membrane (see figure below) is made of a double layer of special lipids, known as **phospholipids**. The phospholipid is a lipid molecule with a hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails. Because of the hydrophilic and hydrophobic nature of the phospholipid, the molecule must be arranged in a specific pattern as only certain parts of the molecule can physically be in contact with water. Remember that there is water outside the cell, and the **cytoplasm** inside the cell is mostly water as well. So the phospholipids are arranged in a double layer (a bilayer) to keep the cell separate from its environment. Lipids do not mix with water (recall that oil is a lipid), so the phospholipid bilayer of the cell membrane acts as a barrier, keeping water out of the cell, and keeping the cytoplasm inside the cell. The cell membrane allows the cell to stay structurally intact in its water-based environment.

The function of the plasma membrane is to control what goes in and out of the cell. Some molecules can go through the cell membrane to enter and leave the cell, but some cannot. The cell is therefore not completely permeable. "Permeable" means that anything can cross a barrier. An open door is completely permeable to anything that wants to enter or exit through the door. The plasma membrane is **semipermeable**, meaning that some things can enter the cell, and some things cannot.

Molecules that cannot easily pass through the bilayer include ions and small hydrophilic molecules, such as glucose, and macromolecules, including proteins and RNA. Examples of molecules that can easily diffuse across the plasma membrane include

carbon dioxide and oxygen gas. These molecules diffuse freely in and out of the cell, along their concentration gradient. Though water is a polar molecule, it can also diffuse through the plasma membrane.

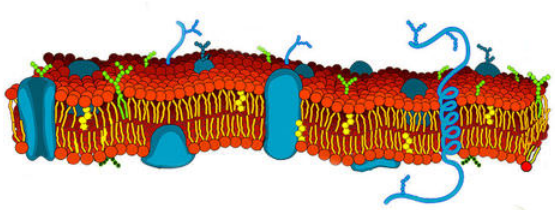


Figure 9.7.2: Plasma membranes are primarily made up of phospholipids (orange). The hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails are shown. The phospholipids form a bilayer (two layers). The middle of the bilayer is an area without water. There can be water on either side of the bilayer. There are many proteins throughout the membrane.

### Cytosol

The inside of all cells also contain a jelly-like substance called **cytosol**. Cytosol is composed of water and other molecules, including **enzymes**, which are proteins that speed up the cell's chemical reactions. Everything in the cell sits in the cytosol, like fruit in a Jell-o mold. The term cytoplasm refers to the cytosol and all of the organelles, the specialized compartments of the cell. The cytoplasm does not include the nucleus. As a prokaryotic cell does not have a nucleus, the DNA is in the cytoplasm.

## Supplemental Resources

- The Plasma Membrane: www.youtube.com/watch?v=moPJkCbKjBs

## Concept Review Exercises

1. What are some of the features of a semipermeable membrane?

2. What do the prefixes hyper, hypo, and iso mean?

## Answers

1. A semipermeable membrane allows some substances to pass through but not others.

2. hyper – higher; hypo – lower; iso - same

## Key Takeaways

- Water moves into and out of cells by osmosis.
- Water (solvent) moves from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water).

## EXERCISES

1. Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

a. Which one has a higher concentration?
b. Which way will water molecules flow?
c. Which volume will increase?
d. Which volume will decrease?
e. What will happen to the concentration of solution A?
f. What will happen to the concentration of solution B?

4. Cells are placed in a solution and the cells then undergo hemolysis. What can be said about the relative concentrations of solute in the cell and the solution?

5. Describe the relative concentrations inside and outside a red blood cell when crenation occurs.

6. A saltwater fish is placed in a freshwater tank. What will happen to the fish? Describe the flow of water molecules to explain the outcome.

### Answers

1. Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

a. Solution B
b. A → → B
c. B
d. A
e. increase
f. decrease

4. Cells contain fluid with higher concentration than solution outside the cell.

5. Cells contain fluid with a lower concentration than the solution outside the cell.

6. Water molecules will flow from the tank water into the fish because the fish has a higher concentration of salt. If the fish absorbs too much water, it will die.

## Contributors

- 
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# 18.S: Solutions (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.*

A **solution** is a homogeneous mixture. The major component is the **solvent**, while the minor component is the **solute**. Solutions can have any phase; for example, an **alloy** is a solid solution. Solutes are **soluble** or **insoluble**, meaning they dissolve or do not dissolve in a particular solvent. The terms **miscible** and **immiscible**, instead of soluble and insoluble, are used for liquid solutes and solvents. The statement *like dissolves like* is a useful guide to predicting whether a solute will dissolve in a given solvent.

The amount of solute in a solution is represented by the **concentration** of the solution. The maximum amount of solute that will dissolve in a given amount of solvent is called the **solubility** of the solute. Such solutions are **saturated**. Solutions that have less than the maximum amount are **unsaturated**. Most solutions are unsaturated, and there are various ways of stating their concentrations. **Mass/mass percent**, **volume/volume percent**, and **mass/volume percent** indicate the percentage of the overall solution that is solute. **Parts per million (ppm)** and **parts per billion (ppb)** are used to describe very small concentrations of a solute. **Molarity**, defined as the number of moles of solute per liter of solution, is a common concentration unit in the chemistry laboratory. **Equivalents** express concentrations in terms of moles of charge on ions. When a solution is diluted, we use the fact that the amount of solute remains constant to be able to determine the volume or concentration of the final diluted solution.

Dissolving occurs by **solvation**, the process in which particles of a solvent surround the individual particles of a solute, separating them to make a solution. For water solutions, the word **hydration** is used. If the solute is molecular, it dissolves into individual molecules. If the solute is ionic, the individual ions separate from each other, forming a solution that conducts electricity. Such solutions are called **electrolytes**. If the dissociation of ions is complete, the solution is a **strong electrolyte**. If the dissociation is only partial, the solution is a **weak electrolyte**. Solutions of molecules do not conduct electricity and are called **nonelectrolytes**.

Solutions have properties that differ from those of the pure solvent. Some of these are **colligative** properties, which are due to the number of solute particles dissolved, not the chemical identity of the solute. Colligative properties include **vapor pressure depression**, **boiling point elevation**, **freezing point depression**, and **osmotic pressure**. Osmotic pressure is particularly important in biological systems. It is caused by **osmosis**, the passage of solvents through certain membranes like cell walls. The **osmolarity** of a solution is the product of a solution's molarity and the number of particles a solute separates into when it dissolves. Osmosis can be reversed by the application of pressure; this reverse osmosis is used to make fresh water from saltwater in some parts of the world. Because of osmosis, red blood cells placed in hypotonic or hypertonic solutions lose function through either hemolysis or crenation. If they are placed in isotonic solutions, however, the cells are unaffected because osmotic pressure is equal on either side of the cell membrane.

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# CHAPTER OVERVIEW

## 19: Acids and Bases

Acids and bases are important classes of chemical compounds. They are part of the foods and beverages we ingest, they are present in medicines and other consumer products, and they are prevalent in the world around us. In this chapter, we will focus on acids and bases and their chemistry.


19.1: Introduction
19.2: Arrhenius Acids and Bases
19.3: Brønsted-Lowry Acids and Bases
19.4: Strong and Weak Acids and Bases and their Salts
19.5: Autoionization of Water
19.6: The pH Scale
19.7: Acid-Base Titrations
19.8: Buffers
19.9: Acids, Bases, pH and Buffers- Questions



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# 19.1: Introduction

Formerly there were rather campy science-fiction television shows in which the hero was always being threatened with death by being plunged into a vat of boiling acid: "Mwa ha ha, Buck Rogers [or whatever the hero's name was], prepare to meet your doom by being dropped into a vat of boiling acid!" (The hero always escapes, of course.) This may have been interesting drama, but not very good chemistry. If the villain knew his/her/its science, the hero would have been dropped into a vat of boiling base.

Recall that the active component of a classic acid is the $H^+$ ion, while the active part of a classic base is the $OH^-$ ion. Both ions are related to water in that all $H^+$ ion needs to become a water molecule is an $OH^-$ ion, while all an $OH^-$ ion needs to become water is an $H^+$ ion. Consider the relative masses involved: an ion of mass 1 needs an ion of mass 17 to make water, while an ion of mass 17 needs an ion of mass 1 to make water. Which process do you think will be easier?

In fact, bases are more potentially dangerous than acids because it is much easier for an $OH^-$ ion to rip off an $H^+$ ion from surrounding matter than it is for an $H^+$ ion to rip off an $OH^-$ ion. Certain household chemicals, such as some brands of cleaner, can be very concentrated bases, which makes them among the most potentially hazardous substances found around the home. If spilled on the skin, these strong caustic compounds can immediately remove $H^+$ ions from the flesh, resulting in chemical burns. Compare this to the fact that we occasionally purposefully ingest substances such as citrus fruits, vinegar, and wine—all of which contain acids. (Of course, some parts of the body, such as the eyes, are extremely sensitive to acids as well as bases.) It seems that our bodies are more capable of dealing with acids than with bases.




Figure **19.1.1** Household chemicals © Thinkstock. On the left is a common acid, and on the right is a common base. Which one is more potentially hazardous?

A note to all of the villains out there...get your chemistry right if you want to be successful!

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## 19.2: Arrhenius Acids and Bases

**Learning Objective**

- Identify an Arrhenius acid and an Arrhenius base.
- Write the chemical reaction between an Arrhenius acid and an Arrhenius base.

Historically, the first chemical definition of an acid and a base was put forward by Svante Arrhenius, a Swedish chemist, in 1884. An **Arrhenius acid** is a compound that increases the $H^+$ ion concentration in an aqueous solution. The $H^+$ ion is just a bare proton, and it is rather clear that bare protons are not floating around in an aqueous solution. Instead, chemistry has defined the **hydronium ion** ($H_3O^+$) as the actual chemical species that represents an $H^+$ ion. $H^+$ ions and $H_3O^+$ ions are often considered interchangeable when writing chemical equations (although a properly balanced chemical equation should also include the additional $H_2O$). Classic Arrhenius acids can be considered ionic compounds in which $H^+$ is the cation. Table **19.2.1** lists some Arrhenius acids and their names.

Table **19.2.1** Some Arrhenius Acids

| Formula | Name |
|---|---|
| $HC_2H_3O_2$ (also written $CH_3COOH$) | acetic acid |
| $HClO_3$ | chloric acid |
| HCl | hydrochloric acid |
| HBr | hydrobromic acid |
| HI | hydriodic acid |
| HF | hydrofluoric acid |
| $HNO_3$ | nitric acid |
| $H_2C_2O_4$ | oxalic acid |
| $HClO_4$ | perchloric acid |
| $H_3PO_4$ | phosphoric acid |
| $H_2SO_4$ | sulfuric acid |
| $H_2SO_3$ | sulfurous acid |

An **Arrhenius base** is a compound that increases the $OH^-$ ion concentration in aqueous solution. Ionic compounds of the $OH^-$ ion are classic Arrhenius bases.

**Example 19.2.1**

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

a. $HNO_3$
b. $CH_3OH$
c. $Mg(OH)_2$

**Solution**

a. This compound is an ionic compound between $H^+$ ions and $NO_3^-$ ions, so it is an Arrhenius acid.
b. Although this formula has an OH in it, we do not recognize the remaining part of the molecule as a cation. It is neither an acid nor a base. (In fact, it is the formula for methanol, an organic compound.)
c. This formula also has an OH in it, but this time we recognize that the magnesium is present as $Mg^{2+}$ cations. As such, this is an ionic compound of the $OH^-$ ion and is an Arrhenius base.

**Exercise 19.2.1**

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. KOH
2. $H_2SO_4$
3. $C_2H_6$

***Answer***

1. Arrhenius base
2. Arrhenius acid
3. neither

Acids have some properties in common. They turn litmus, a plant extract, red. They react with some metals to give off $H_2$ gas. They react with carbonate and hydrogen carbonate salts to give off $CO_2$ gas. Acids that are ingested typically have a sour, sharp taste. (The name *acid* comes from the Latin word *acidus*, meaning "sour.") Bases also have some properties in common. They are slippery to the touch, turn litmus blue, and have a bitter flavor if ingested.

Acids and bases have another property: they react with each other to make water and an ionic compound called a salt. A **salt**, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a **neutralization reaction** and can be represented as:

$$\text{acid} + \text{base} \rightarrow H_2O + \text{salt}$$

The stoichiometry of the balanced chemical equation depends on the number of $H^+$ ions in the acid and the number of $OH^-$ ions in the base.

**Example 19.2.2**

Write the balanced chemical equation for the neutralization reaction between $H_2SO_4$ and KOH. What is the name of the salt that is formed?

**Solution**

The general reaction is as follows:

$$H_2SO_4 + KOH \rightarrow H_2O + \text{salt}$$

Because the acid has two $H^+$ ions in its formula, we need two $OH^-$ ions to react with it, making two $H_2O$ molecules as product. The remaining ions, $K^+$ and $SO_4^{2-}$, make the salt potassium sulfate ($K_2SO_4$). The balanced chemical reaction is as follows:

$$H_2SO_4 + 2KOH \rightarrow 2H_2O + K_2SO_4$$

**? Exercise 19.2.2**

Write the balanced chemical equation for the neutralization reaction between HCl and $Mg(OH)_2$. What is the name of the salt that is formed?

**Answer**

$2HCl + Mg(OH)_2 \rightarrow 2H_2O + MgCl_2$; magnesium chloride

## Key Takeaways

- An Arrhenius acid is a compound that increases the $H^+$ ion concentration in aqueous solution.
- An Arrhenius base is a compound that increases the $OH^-$ ion concentration in aqueous solution.
- The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.

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# 19.3: Brønsted-Lowry Acids and Bases

**Learning Objectives**

- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

The Arrhenius definition of acid and base is limited to aqueous (that is, water) solutions. Although this is useful because water is a common solvent, it is limited to the relationship between the $H^+$ ion and the $OH^-$ ion. What would be useful is a general definition more applicable to other chemical reactions and, importantly, independent of $H_2O$.

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton ($H^+$) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor (PD), while a Brønsted-Lowry base is a proton acceptor (PA).

It is easy to see that the Brønsted-Lowry definition covers the Arrhenius definition of acids and bases. Consider the prototypical Arrhenius acid-base reaction:

$$\underset{\text{acid}}{H^+(aq)} + \underset{\text{base}}{OH^-(aq)} \rightarrow H_2O\,(l)$$

Acid species and base species are marked. The proton, however, is (by definition) a proton donor (labeled PD), while the $OH^-$ ion is acting as the proton acceptor (labeled PA):

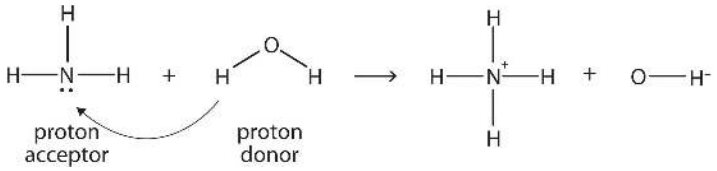
$$\underset{PD}{H^+(aq)} + \underset{PA}{OH^-(aq)} \rightarrow H_2O\,(l)$$

The proton donor is a Brønsted-Lowry acid, and the proton acceptor is the Brønsted-Lowry base:

$$\underset{\text{BL acid}}{H^+(aq)} + \underset{\text{BL base}}{OH^-(aq)} \rightarrow H_2O\,(l)$$

Thus $H^+$ is an acid by both definitions, and $OH^-$ is a base by both definitions.

Ammonia ($NH_3$) is a base even though it does not contain $OH^-$ ions in its formula. Instead, it generates $OH^-$ ions as the product of a proton-transfer reaction with $H_2O$ molecules; $NH_3$ acts like a Brønsted-Lowry base, and $H_2O$ acts like a Brønsted-Lowry acid:




A reaction with water is called **hydrolysis**; we say that $NH_3$ hydrolyzes to make $NH_4^+$ ions and $OH^-$ ions.

Even the dissolving of an Arrhenius acid in water can be considered a Brønsted-Lowry acid-base reaction. Consider the process of dissolving HCl(g) in water to make an aqueous solution of hydrochloric acid. The process can be written as follows:

$$HCl\,(g) + H_2O(\ell) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)$$

HCl(g) is the proton donor and therefore a Brønsted-Lowry acid, while $H_2O$ is the proton acceptor and a Brønsted-Lowry base. These two examples show that $H_2O$ can act as both a proton donor and a proton acceptor, depending on what other substance is in the chemical reaction. A substance that can act as a proton donor or a proton acceptor is called **amphiprotic**. Water is probably the most common amphiprotic substance we will encounter, but other substances are also amphiprotic.

### Example 19.3.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$C_6H_5OH + NH_2^- \longrightarrow C_6H_5O^- + NH_3$$

**Solution**

The $C_6H_5OH$ molecule is losing an $H^+$; it is the proton donor and the Brønsted-Lowry acid. The $NH_2^-$ ion (called the amide ion) is accepting the $H^+$ ion to become $NH_3$, so it is the Brønsted-Lowry base.

### Exercise 19.3.1: Aluminum Ions in Solution

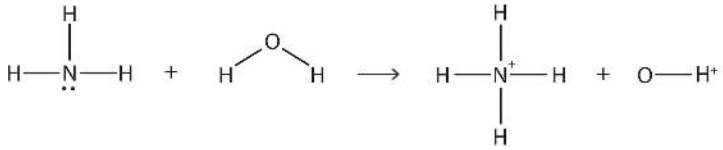
Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+$$

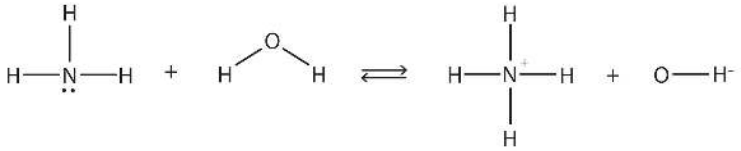
**Answer**

Brønsted-Lowry acid: $Al(H_2O)_6^{3+}$; Brønsted-Lowry base: $H_2O$

In the reaction between $NH_3$ and $H_2O$,



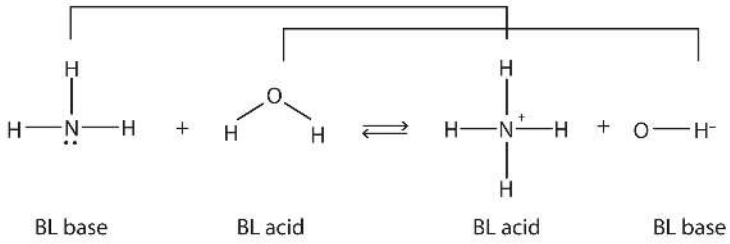
the chemical reaction does not go to completion; rather, the reverse process occurs as well, and eventually the two processes cancel out any additional change. At this point, we say the chemical reaction is at *equilibrium*. Both processes still occur, but any net change by one process is countered by the same net change of the other process; it is a *dynamic*, rather than a *static*, equilibrium. Because both reactions are occurring, it makes sense to use a double arrow instead of a single arrow:



What do you notice about the reverse reaction? The $NH_4^+$ ion is donating a proton to the $OH^-$ ion, which is accepting it. This means that the $NH_4^+$ ion is acting as the proton donor, or Brønsted-Lowry acid, while the $OH^-$ ion, the proton acceptor, is acting as a Brønsted-Lowry base. The reverse reaction is also a Brønsted-Lowry acid base reaction:

BL bases. NH4+ and H2O are the BL acids. lt-chem-64081" style="width: 750px; height: 173px;" width="750px" height="173px" src="/@api/deki/files/92035/3765cabac9591a0fb3dd5878f56075e2.jpg" data-quail-id="174">

This means that both reactions are acid-base reactions by the Brønsted-Lowry definition. If you consider the species in this chemical reaction, two sets of similar species exist on both sides. Within each set, the two species differ by a proton in their formulas, and one member of the set is a Brønsted-Lowry acid, while the other member is a Brønsted-Lowry base. These sets are marked here:




The two sets—$NH_3/NH_4^+$ and $H_2O/OH^-$—are called **conjugate acid-base pairs**. We say that $NH_4^+$ is the conjugate acid of $NH_3$, $OH^-$ is the conjugate base of $H_2O$, and so forth. Every Brønsted-Lowry acid-base reaction can be labeled with two conjugate acid-base pairs.

### Example 19.3.2

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 19.3.2

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)

### Chemistry is Everywhere: 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 HCl(aq). In Section 4.6, vinegar was 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 $NH_3$, which is found in numerous cleaning products. $NH_3$ is a base because it increases the $OH^-$ ion concentration by reacting with $H_2O$:

$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from $H_2O$ and forming excess $OH^-$ ions. This is one explanation for why soap solutions are slippery.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for NaOH, although it is also used as a synonym for KOH. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and clog a water pipe. Unfortunately, lye can also attack body 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, non-lye drain cleaners (like the one in the accompanying figure) use peroxide compounds to react on the materials in the clog and clear the drain.




Figure **19.3.1** Drain Cleaners. Drain cleaners can be made from a reactive material that is less caustic than a base. Source: Photo used by permission of Citrasolv, LLC.

## Key Takeaways

- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor.
- Acid-base reactions include two sets of conjugate acid-base pairs.

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# 19.4: Strong and Weak Acids and Bases and their Salts

**Learning Objectives**

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.
- Determine if a salt produces an acidic or a basic solution.

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 $\mathbf{HCl\,(aq)}$. When $\mathbf{HCl}$ is dissolved in $\mathbf{H_2O}$, it completely dissociates into $\mathbf{H^+\,(aq)}$ and $\mathbf{Cl^-\,(aq)}$ ions; all the $\mathbf{HCl}$ molecules become ions:

$$\mathbf{HCl \xrightarrow{100\,\%} H^+(aq) + Cl^-(aq)}$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. Acetic acid ( $\mathbf{HC_2H_3O_2}$) is an example of a weak acid:

$$\mathbf{HC_2H_3O_2 \xrightarrow{\sim 5\,\%} H^+(aq) + C_2H_3O_2^-(aq)}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as a reversible reaction:

$$\mathbf{HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)}$$

As it turns out, there are very few strong acids, which are given in Table **19.4.1**. 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.

Table **19.4.1**: Strong Acids and Bases

| Acids | Bases |
|---|---|
| HCl | LiOH |
| HBr | NaOH |
| HI | KOH |
| $HNO_3$ | RbOH |
| $H_2SO_4$ | CsOH |
| $HClO_3$ | $Mg(OH)_2$ |
| $HClO_4$ | $Ca(OH)_2$ |
| | $Sr(OH)_2$ |
| | $Ba(OH)_2$ |

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 **19.4.1**); any base not listed is a weak base. All strong bases are $OH^-$ compounds. So a base dependent on some other mechanism, such as $NH_3$ (which does not contain $OH^-$ ions as part of its formula), will be a weak base.

**Example 19.4.1**

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. $C_5H_5N$

**Solution**

a. Because HCl is listed in Table 19.4.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 19.4.1, 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 19.4.1**

Identify each acid or base as strong or weak.

a. RbOH
b. $HNO_2$

**Answer a**

strong base

**Answer b**

weak acid

**✓ Example 19.4.2**

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:

$$Ca(OH)_2 \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$$

Because $Ca(OH)_2$ is listed in Table 19.4.1, this reaction proceeds 100% to products.

**? Exercise 19.4.2**

Write the balanced chemical equation for the dissociation of hydrazoic acid ($HN_3$) and indicate whether it proceeds 100% to products or not.

**Answer**

The reaction is as follows:

$$HN_3 \longrightarrow H^+(aq) + N_3^-(aq)$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Certain salts will also affect the acidity or basicity of aqueous solutions because some of the ions will undergo hydrolysis, just like $NH_3$ does, to make a basic solution. The general rule is that salts with ions that are part of strong acids or bases will not hydrolyze, while salts with ions that are part of weak acids or bases will hydrolyze.

Consider NaCl. When it dissolves in an aqueous solution, it separates into $Na^+$ ions and $Cl^-$ ions:

$$NaCl \longrightarrow Na^+(aq) + Cl^-(aq)$$

Will the $Na^+(aq)$ ion hydrolyze? If it does, it will interact with the $OH^-$ ion to make NaOH:

$$Na^+(aq) + H_2O \longrightarrow NaOH + H^+(aq)$$

However, NaOH is a strong base, which means that it is 100% ionized in solution:

$$NaOH \longrightarrow Na^+(aq) + OH^-(aq)$$

The free $OH^-(aq)$ ion reacts with the $H^+(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the $Na^+(aq)$ ion. What about the $Cl^-$ ion? Will it hydrolyze? If it does, it will take an $H^+$ ion from a water molecule:

$$Cl^-(aq) + H_2O \longrightarrow HCl + OH^-$$

However, HCl is a strong acid, which means that it is 100% ionized in solution:

$$HCl \longrightarrow H^+(aq) + Cl^-(aq)$$

The free $H^+(aq)$ ion reacts with the $OH^-(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the $Cl^-(aq)$ ion. Because neither ion in NaCl affects the acidity or basicity of the solution, NaCl is an example of a neutral salt. A neutral salt is any ionic compound that does not affect the acidity or basicity of its aqueous solution.

Things change, however, when we consider a salt like $NaC_2H_3O_2$. We already know that the $Na^+$ ion won't affect the acidity of the solution. What about the acetate ion? If it hydrolyzes, it will take an $H^+$ from a water molecule:

$$C_2H_3O_2^-(aq) + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-(aq)$$

Does this happen? Yes, it does. Why? *Because $HC_2H_3O_2$ is a weak acid.* Any chance a weak acid has to form, it will (the same with a weak base). As some $C_2H_3O_2^-$ ions hydrolyze with $H_2O$ to make the molecular weak acid, $OH^-$ ions are produced. $OH^-$ ions make solutions basic. Thus $NaC_2H_3O_2$ solutions are slightly basic, so such a salt is called a **basic salt**.

There are also salts whose aqueous solutions are slightly acidic. $NH_4Cl$ is an example. When $NH_4Cl$ is dissolved in $H_2O$, it separates into $NH_4^+$ ions and $Cl^-$ ions. We have already seen that the $Cl^-$ ion does not hydrolyze. However, the $NH_4^+$ ion will:

$$NH_4^+(aq) + H_2O \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Recall from Section 12.2, that $H_3O^+$ ion is the hydronium ion, the more chemically proper way to represent the $H^+$ ion. This is the classic acid species in solution, so a solution of $NH_4^+(aq)$ ions is slightly acidic. $NH_4Cl$ is an example of an **acid salt**. The molecule $NH_3$ is a weak base, and it will form when it can, just like a weak acid will form when it can.

So there are two general rules:

1. If an ion derives from a strong acid or base, it will not affect the acidity of the solution.
2. If an ion derives from a weak acid, it will make the solution basic; if an ion derives from a weak base, it will make the solution acidic.

### ✔ Example 19.4.3

Identify each salt as acidic, basic, or neutral.

a. KCl
b. $KNO_2$
c. $NH_4Br$

**Solution**

a. The ions from KCl derive from a strong acid (HCl) and a strong base (KOH). Therefore, neither ion will affect the acidity of the solution, so KCl is a neutral salt.
b. Although the $K^+$ ion derives from a strong base (KOH), the $NO_2^-$ ion derives from a weak acid ($HNO_2$). Therefore the solution will be basic, and $KNO_2$ is a basic salt.

c. Although the $Br^-$ ions derive from a strong acid (HBr), the $NH_4^+$ ion derives from a weak base ($NH_3$), so the solution will be acidic, and $NH_4Br$ is an acidic salt.

**? Exercise 19.4.3**

Identify each salt as acidic, basic, or neutral.

A. $(C_5H_5NH)Cl$
B. $Na_2SO_3$

**Answer a**

acidic

**Answer b**

basic

Some salts are composed of ions that come from both weak acids and weak bases. The overall effect on an aqueous solution depends on which ion exerts more influence on the overall acidity. We will not consider such salts here.

## Summary

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.
- Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.

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# 19.5: Autoionization of Water

**Learning Objectives**

- Describe the autoionization of water.
- Calculate the concentrations of $H^+$ and $OH^-$ in solutions, knowing the other concentration.

We have already seen that $H_2O$ can act as an acid or a base:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \text{ } (H_2O \text{ acts as an acid})$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \text{ } (H_2O \text{ acts as a base})$$

It may not be surprising to learn, then, that within any given sample of water, some $H_2O$ molecules are acting as acids, and other $H_2O$ molecules are acting as bases. The chemical equation is as follows:

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

This occurs only to a very small degree: only about 6 in $10^8$ $H_2O$ molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both $H^+(aq)$ and $OH^-(aq)$ in a sample of pure $H_2O$ is about $1.0 \times 10^{-7}$ M. If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

for *any* sample of pure water because $H_2O$ can act as both an acid and a base. The product of these two concentrations is $1.0 \times 10^{-14}$:

$$[H^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

In acids, the concentration of $H^+(aq)$—$[H^+]$—is greater than $1.0 \times 10^{-7}$ M, while for bases the concentration of $OH^-(aq)$—$[OH^-]$—is greater than $1.0 \times 10^{-7}$ M. However, the *product* of the two concentrations—$[H^+][OH^-]$—is *always* equal to $1.0 \times 10^{-14}$, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted $K_W$:

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$ has to be for the product to equal $1.0 \times 10^{-14}$, 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 $K_W$.

**Example 19.5.1**

What is $[OH^-]$ of an aqueous solution if $[H^+]$ is $1.0 \times 10^{-4}$ M?

**Solution**

Using the expression and known value for $K_W$,

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[OH^-]$$

We solve by dividing both sides of the equation by $1.0 \times 10^{-4}$:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$$

It is assumed that the concentration unit is molarity, so $[OH^-]$ is $1.0 \times 10^{-10}$ M.

**Exercise 19.5.1**

What is $[H^+]$ of an aqueous solution if $[OH^-]$ is $1.0 \times 10^{-9}$ M?

**Answer**

$1.0 \times 10^{-5}$ M

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of $H^+$ or $OH^-$ ions in the formula unit because $[H^+]$ or $[OH^-]$ may not be the same as the concentration of the acid or base itself.

**Example 19.5.2**

What is $[H^+]$ in a 0.0044 M solution of $Ca(OH)_2$?

**Solution**

We begin by determining $[OH^-]$. The concentration of the solute is 0.0044 M, but because $Ca(OH)_2$ is a strong base, there are two $OH^-$ ions in solution for every formula unit dissolved, so the actual $[OH^-]$ is two times this, or $2 \times 0.0044$ M = 0.0088 M. Now we can use the $K_W$ expression:

$$[H^+][OH^-] = 1.0 \times 10^{-14} = [H^+](0.0088 \text{ M})$$

Divide both sides by 0.0088:

$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12} M$$

$[H^+]$ has decreased significantly in this basic solution.

**Exercise 19.5.2**

What is $[OH^-]$ in a 0.00032 M solution of $H_2SO_4$? (Hint: assume both $H^+$ ions ionize.)

***Answer***

$1.6 \times 10^{-11}$ M

For strong acids and bases, $[H^+]$ and $[OH^-]$ can be determined directly from the concentration of the acid or base itself because these ions are 100% ionized by definition. However, for weak acids and bases, this is not so. The degree, or percentage, of ionization would need to be known before we can determine $[H^+]$ and $[OH^-]$.

**Example 19.5.3**

A 0.0788 M solution of $HC_2H_3O_2$ is 3.0% ionized into $H^+$ ions and $C_2H_3O_2^-$ ions. What are $[H^+]$ and $[OH^-]$ for this solution?

**Solution**

Because the acid is only 3.0% ionized, we can determine $[H^+]$ from the concentration of the acid. Recall that 3.0% is 0.030 in decimal form:

$[H^+] = 0.030 \times 0.0788 = 0.00236$ M

With this $[H^+]$, then $[OH^-]$ can be calculated as follows:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.00236} = 4.2 \times 10^{-12} M$$

This is about 30 times higher than would be expected for a strong acid of the same concentration.

## Exercise 19.5.3

A 0.0222 M solution of pyridine ($C_5H_5N$) is 0.44% ionized into pyridinium ions ($C_5H_5NH^+$) and $OH^-$ ions. What are $[OH^-]$ and $[H^+]$ for this solution?

**Answer**

$[OH^-] = 9.77 \times 10^{-5}$ M; $[H^+] = 1.02 \times 10^{-10}$ M

## Summary

In any aqueous solution, the product of [H+] and [OH−] equals $\mathbf{1.0 \times 10^{-14}}$ (at room temperature).

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# 19.6: The pH Scale

**Learning Objectives**

- Define *pH*.
- Determine the pH of acidic and basic solutions.

As we have seen, $[H^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

**pH** is commonly defined as a logarithmic function of $[H^+]$:

$$\mathbf{pH = -\log[H^+]} \tag{19.6.1}$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scale and is the range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to quickly determine whether a given aqueous solution is acidic, basic, or neutral.

**Example 19.6.1**

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

**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 19.6.1**

Identify each substance as acidic, basic, or neutral based only on the stated pH.

1. human blood, pH = 7.4
2. household ammonia, pH = 11.0
3. cherries, pH = 3.6

**Answers**

1. basic
2. basic
3. acidic

Table **19.6.1** gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.

Table **19.6.1** Typical pH Values of Various Substances*

| Substance | pH |
|---|---|
| stomach acid | 1.7 |
| lemon juice | 2.2 |
| vinegar | 2.9 |
| soda | 3.0 |
| wine | 3.5 |
| coffee, black | 5.0 |
| milk | 6.9 |
| pure water | 7.0 |
| blood | 7.4 |
| seawater | 8.5 |
| milk of magnesia | 10.5 |
| ammonia solution | 12.5 |
| 1.0 M NaOH | 14.0 |
| *Actual values may vary depending on conditions | |

pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the $[H^+]$ as a solution with a pH of 2.0, which in turn has 10 times the $[H^+]$ as a solution with a pH of 3.0 and so forth.

Using the definition of pH (Equation 19.6.1), it is also possible to calculate $[H^+]$ (and $[OH^-]$) from pH and vice versa. The general formula for determining $[H^+]$ from pH is as follows:

$$[H^+] = 10^{-pH}$$

## Key Takeaways

- pH is a logarithmic function of $[H^+]$.
- $[H^+]$ can be calculated directly from pH.
- pOH is related to pH and can be easily calculated from pH.

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# 19.7: Acid-Base Titrations

**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 19.7.1). 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 19.7.1 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 19.7.1**

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:

# moles $HNO_3$ = (0.04402 L)(0.0885 M) = 0.00390 mol $HNO_3$

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390\ \cancel{mol\ HNO_3} \times \frac{1\ mol\ Ca(OH)_2}{2\ \cancel{mol\ HNO_3}} = 0.00195\ mol\ Ca(OH)_2$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195\ \cancel{mol\ Ca(OH)_2} \times \frac{74.1\ g\ Ca(OH)_2}{\cancel{mol\ Ca(OH)_2}} = 0.144\ g\ Ca(OH)_2$$

**? Exercise 19.7.1**

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$H_2C_2O_4 + 2\,NaOH \longrightarrow Na_2C_2O_4 + 2\,H_2O$$

**Answer**

0.182 g

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.

## Summary

A titration is the quantitative reaction of an acid and a base. Indicators are used to show that all of the analyte has reacted with the titrant.

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# 19.8: Buffers

**Learning Objectives**

- Define *buffer*.
- Correctly identify the two components of a buffer.

As indicated in Section 12.5, weak acids are relatively common, even in the foods we eat. But we occasionally encounter a strong acid or base, such as stomach acid, which has a strongly acidic pH of 1.7. By definition, strong acids and bases can produce a relatively large amount of $H^+$ or $OH^-$ ions and consequently have marked chemical activities. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [approximated as 0.1 M HCl(aq)] were added to the bloodstream and no correcting mechanism were present, the pH of the blood would decrease from about 7.4 to about 4.7—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

This mechanism involves a **buffer**, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid, or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved $HC_2H_3O_2$ (a weak acid) and $NaC_2H_3O_2$ (the salt derived from that weak acid). Another example of a buffer is a solution containing $NH_3$ (a weak base) and $NH_4Cl$ (a salt derived from that weak base).

Let us use an $HC_2H_3O_2/NaC_2H_3O_2$ buffer to demonstrate how buffers work. If a strong base—a source of $OH^-(aq)$ ions—is added to the buffer solution, those $OH^-$ ions will react with the $HC_2H_3O_2$ in an acid-base reaction:

$$\mathbf{HC_2H_3O_2\,(aq) + OH^-\,(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-\,(aq)} \tag{19.8.1}$$

Rather than changing the pH dramatically by making the solution basic, the added $OH^-$ ions react to make $H_2O$, so the pH does not change much.

If a strong acid—a source of $H^+$ ions—is added to the buffer solution, the $H^+$ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of $H^+$ ions and $C_2H_3O_2^-$ ions are present in the same solution, they will come together to make $HC_2H_3O_2$:

$$\mathbf{H^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq)} \tag{19.8.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added $H^+$ ions react to make molecules of a weak acid. Figure **19.8.1** illustrates both actions of a buffer.

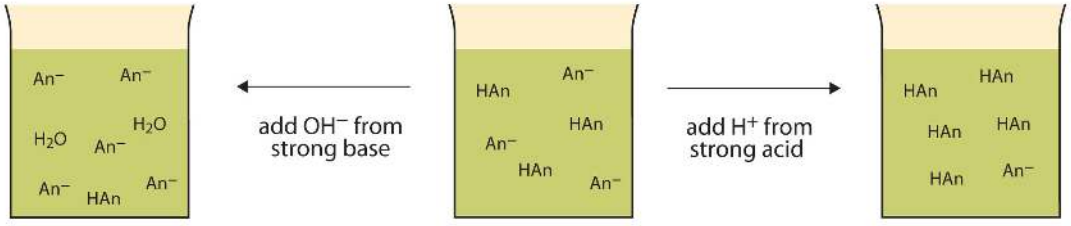



Figure **19.8.1** The Actions of Buffers. Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing $NH_3$ and $NH_4Cl$, $NH_3$ molecules can react with any excess $H^+$ ions introduced by strong acids:

$$\mathbf{NH_3\,(aq) + H^+\,(aq) \rightarrow NH_4^+\,(aq)} \tag{19.8.3}$$

while the **ammonium ion** ($\mathbf{NH_4^+\,(aq)}$) can react with any hydroxide ions introduced by strong bases:

$$\mathbf{NH_4^+\,(aq) + OH^-\,(aq) \rightarrow NH_3\,(aq) + H_2O(\ell)} \tag{19.8.4}$$

**Example 19.8.1:**

Which combinations of compounds can make a buffer solution?

1. $HCHO_2$ and $NaCHO_2$
2. HCl and NaCl
3. $CH_3NH_2$ and $CH_3NH_3Cl$
4. $NH_3$ and NaOH

**Solution**

1. $HCHO_2$ is formic acid, a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid (the formate ion [$CHO_2^-$]). The combination of these two solutes would make a buffer solution.
2. HCl is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
3. $CH_3NH_2$ is methylamine, which is like $NH_3$ with one of its H atoms substituted with a $CH_3$ group. Because it is not listed in Table **19.8.1**, we can assume that it is a weak base. The compound $CH_3NH_3Cl$ is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
4. $NH_3$ is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

**Exercise 19.8.1**

Which combinations of compounds can make a buffer solution?

1. $NaHCO_3$ and NaCl
2. $H_3PO_4$ and $NaH_2PO_4$
3. $NH_3$ and $(NH_4)_3PO_4$
4. NaOH and NaCl

**Answer a**

No. Need a weak acid or base and a salt of its conjugate base or acid.

**Answer b**

Yes. Need a weak acid or base and a salt of its conjugate base or acid.

**Answer c**

Yes.

**Answer d**

No. Need a weak base and weak acid.

Buffers work well only for limited amounts of added strong acid or base. Once either solute is completely reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more initial solute dissolved within them have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of $HCO_3^-$ and $H_2CO_3$ [the second compound is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

**Food and Drink Application: the Acid that Eases Pain**

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table **19.8.1**, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

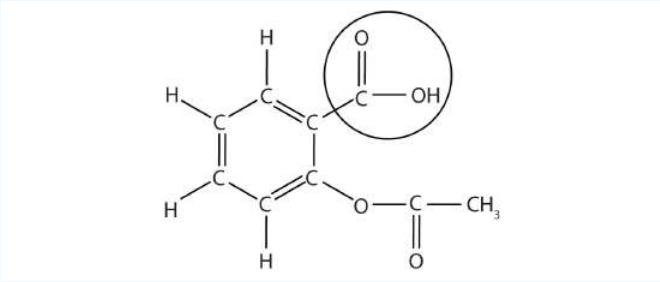



Figure **19.8.2**: The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent—usually MgO—that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects—gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin will remain on the market.

## Summary

A buffer is a solution that resists sudden changes in pH.

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# 19.9: Acids, Bases, pH and Buffers- Questions

**Sacramento City College**
**CHEM 309: General, Organic and Biochemistry**
**Prof. Dianne Bennett**



Template:HideTOC

ALL questions listed must be answered to earn credit for completing the text homework. Yes, even the Additional Exercises if applicable.

## Properties of Acids and Bases

**(01) According to the Arrhenius definition of acids, an acid gives off what in solution?**

**According to the Bronsted-Lowry, what is the definition of an acid? What is the definition of a base?**

**(02) For every given acid or base, write the equation of their reactions with water when they donate or accept one hydrogen ion.**

a. Hydrocyanic acid
b. Carbonate ion
c. Ammonium ion
d. Sulfuric acid
e. Acetic acid

## Conjugate Acids and Bases

**(03) For each of the following acids, determine the form of their conjugate bases.**

a. $HSO_4^-$
b. $H_2CO_3$
c. HF
d. $HPO_4^{2-}$
e. HCOOH

**(04) For each of the following bases, determine the form of their conjugate acids.**

a. $Br^-$
b. $NO_3^-$
c. $S^{2-}$
d. $NH_3$
e. $HCO_3^-$

## Strengths of Acids and Bases

**(05) Nitric acid, $HNO_3$, is a strong acid. Define 'strong' acid, and write the equation of nitric acid reacting with water. How does this equation differ from the reaction of a weak acid, such as hydrosulfuric acid ($H_2S$)? Sketch the reaction of hydrosulfuric acid with water to see the difference clearly.**

**(06) Lithium hydroxide, LiOH, is a strong base. Define 'strong base' and write the equation of lithium hydroxide reacting with water. Sketch an example of the reaction of a weak base with water and compare it to the strong base reaction. How do**

**they differ?**

**(07) Phosphoric acid is one of the few acids that has three acidic hydrogens, and is called 'triprotic'. Write a chemical equation for phosphoric acid reacting with water and losing one of its hydrogens. Using the products from the first equation, write another equation to show the second hydrogen being lost. Continue in this fashion to show the last hydrogen being lost.**

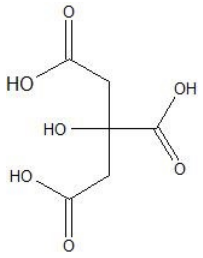
**(08) For each chemical reaction, determine whether they are representative of the dissociation reaction of a strong acid, a weak acid, a strong base, or a weak base.**

a. $Na(OH)_{(aq)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$
b. $HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$
c. $H_2PO^-_{4\ (aq)} + H_2O_{(l)} \rightleftharpoons H_3PO_{4\ (aq)} + OH^-_{(aq)}$
d. $H_2PO^-_{4\ (aq)} + H_2O_{(l)} \rightleftharpoons HPO^{2-}_{4\ (aq)} + H_3O^+_{(aq)}$
e. $HCl_{(aq)} + H_2O_{(l)} \rightarrow Cl^-_{(aq)} + H_3O^+_{(aq)}$

**(09) Perform the dissociation reactions for each of the given acids. Use the reaction arrow to tell whether they are strong acids or weak acids. For diprotic acids, show the loss of the first hydrogen ion. Hint: What are the six strong acids?**

a. $HClO_4$
b. HSCN
c. HBr
d. $H_2CO_3$
e. $CH_3COOH$

**(10) Study the following structure of citric acid. How many acidic groups are contained in this molecule? Circle the acidic hydrogens that can be removed by interactions with bases. Write the three consecutive dissociation reactions using bond-line structures, one reaction for each hydrogen being removed (one at a time).**




## Acid-Base Equilibria

**(11) What is occurring when a reaction is said to be in equilibrium? Write an equation in which** water **is in equilibrium with a proton and hydroxide. Are the concentrations changing when they are in equilibrium or do they remain constant? Why is using the double-arrows to separate products from reactants so important in equilibrium reactions?**

## Le Chatelier's Principle

**(12) Observe the following reaction and answer the questions beneath.**

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)} \tag{19.9.1}$$

a. What will the effect on the equilibrium be if the concentration of hydronium ions is increased?
b. What will the effect on the equilibrium be if the concentration of acetate is decreased?
c. If you increase the concentration of water, will the equilibrium shift left or right?
d. If you decrease the concentration of acetic acid, will the equilibrium shift left or right?

**(13) A generic example of an equilibrium reaction is shown below. Answer the following questions about what direction equilibrium shift according to Le Chatelier's principle.**

$$A + B \rightleftharpoons C + D + \text{heat} \tag{19.9.2}$$

a. Removing some of compound $A$
b. Increasing the temperature
c. Adding more of compound $D$
d. Increasing concentration of compound $B$
e. Decreasing the temperature

**(14) Some processes involve multiple equilibrium equations put together. For example, the carbonation effect that creates soda water involves more than one set of compounds separated by equilibrium arrows, as shown below.**

$$CO_{2\,(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3\,(aq)} \rightleftharpoons HCO^-_{3\,(aq)} + H^+_{(aq)} \tag{19.9.3}$$

**a. During hypoventilation, what happens to the hydrogen ion concentration?**

**b. During hyperventilation, what happens to the hydrogen ion concentration?**

## Acid-Base Neutralization Reactions

**(15) Write out the neutralization reactions for the following pairs. Make sure to balance the equations as necessary.**

a. $Ba(OH)_2$ and $HNO_3$

b. $Ca(OH)_2$ and $H_2SO_4$

c. $RbOH$ and $HI$

d. $KOH$ and $HClO_4$

e. $Mg(OH)_2$ and $HBr$

## pH

**(16) Examine the following pH measures and tell whether they are in the range to be considered acidic, basic or neutral.**

a. 6.8
b. 13.5
c. 1.9
d. 4.2
e. 9.7

**(17) Using the formula for converting concentration into pH, determine whether each of the following molarities are acidic, basic or neutral. Remember, -log[$H^+$]**

a. $1.0 \times 10^{-7}$ M $H^+$
b. $4.7 \times 10^{-12}$ M $H^+$
c. $6.4 \times 10^{-4}$ M $H^+$
d. $7.3 \times 10^{-10}$ M $H^+$
e. $9.8 \times 10^{-2}$ M $H^+$

**(18) Fill in the blank portions of the table.**

| $[H_3O^+]$ | $[OH^-]$ | pH | Acidic, Basic or Neutral |
|---|---|---|---|
| $1.0 \times 10^{-1}$ | | | |
| | $1.0 \times 10^{-4}$ | | |
| $1.0 \times 10^{-7}$ | | | |
| | $1.0 \times 10^{-9}$ | | |
| $1.0 \times 10^{-13}$ | | | |

**(19) Given the following sets of information, calculate the requested quantities for each problem.**

a. $[H_3O^+] = 4.1 \times 10^{-4}$ M. Find pH, and $[OH^-]$
b. $[OH^-] = 6.6 \times 10^{-9}$ M. Find pOH, and $[H_3O^+]$
c. pH = 9.0. Find $[H_3O^+]$, $[OH^-]$ and pOH
d. pOH = 12.5. Find $[OH^-]$, and $[H_3O^+]$
e. pOH = 7.0. Find $[H_3O^+]$, $[OH^-]$ and pH

## Buffers

**(20) What is the definition of a buffer solution? Determine whether or not each pair below can be used to prepare a buffer solution.**

a. HI and $H_2SO_4$
b. $CH_3COOH$ and $CH_3COOK$
c. $Ca(OH)_2$ and $H_2O$
d. acetic acid and methylamine
e. $NH_3$ and $HNO_3$

**(21) Carbonic acid and bicarbonate ion are an conjugate aicd-base pairs. For each of the following compounds, would the carbonic acid or bicarbonate be more likely to react with them and serve as a buffer to prevent pH change?**

a. HBr
b. LiOH
c. $NH_4^+$
d. $HCOO^-$
e. $CH_3NH_2$

**(22) A person who spends a day swimming and diving underwater requires them to hold their breath for long stretches and to do this repeatedly. This is a contrast to the condition of hyperventilation where breaths are taken rapidly. If a person is holding in their inhaled breaths with few breaks in between, what effect does this have on the $CO_2$ levels in their body? Do they increase or decrease? What effect does this increase or decrease have on the pH of the bloodstream?**

$$CO_{2\,(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3\,(aq)} \rightleftharpoons HCO^-_{3\,(aq)} + H^+_{(aq)} \tag{19.9.4}$$

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