CHEM 110: INTRODUCTORY CHEMISTRY



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CHEM 110: Introductory Chemistry

Spring 2023

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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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1.0: 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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1.1: 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 1.1.1). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.

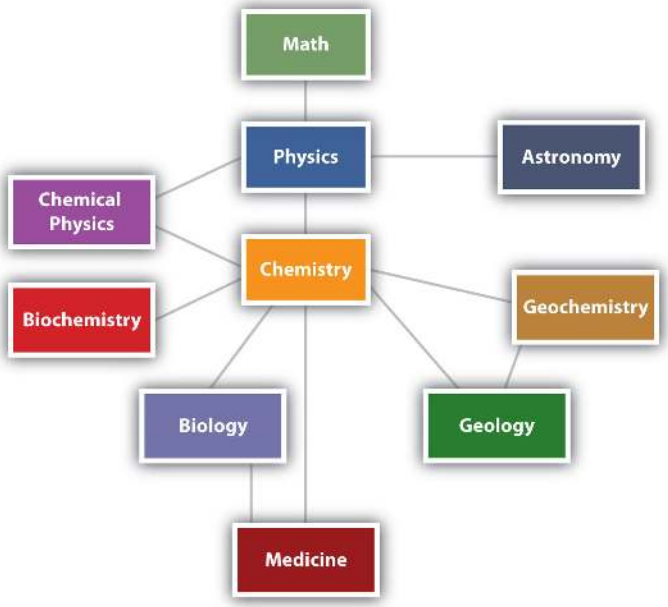


Figure 1.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure 1.1.1 shows how many of the individual fields of science are related.

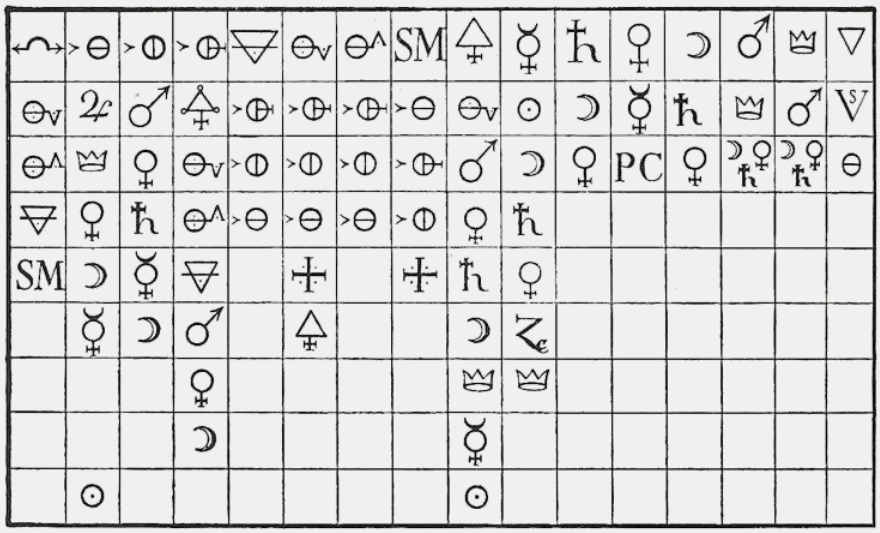
> *There are many other fields of science in addition to the ones listed here.*

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 1.1.1

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 1.1.2

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 1.1.2:

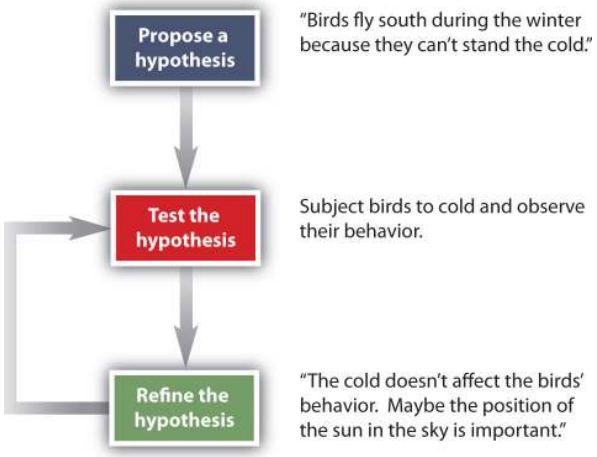


Figure 1.1.2: The General Steps of the Scientific Method. After an observation is made or a question is identified, a hypothesis is made and experiments are designed to test the hypothesis.

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.

1.1.3Exercise

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.

1.1.4Exercise

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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1.2: 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 1.2.1: (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 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 1.2.2).

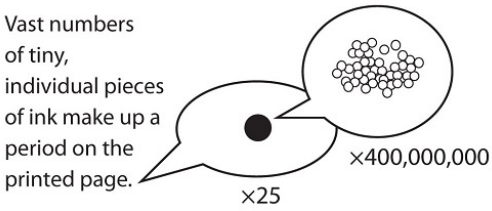


Figure 1.2.2: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The ×25 and ×400,000,000 indicate the 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 1.2.1

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 1.2.2

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.

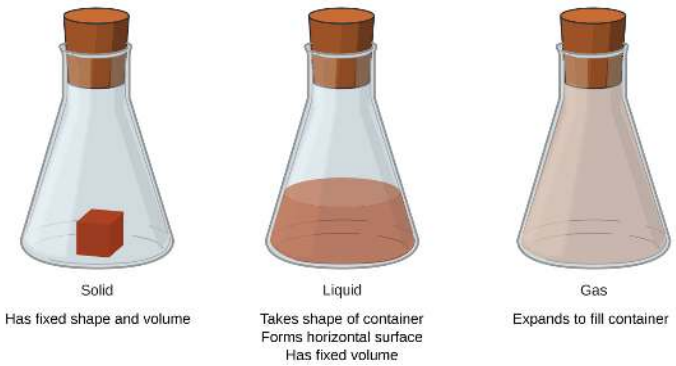


Figure 1.2.3: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

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

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 1.2.2).



Figure 1.2.5: 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 1.2.5). Phase changes are identified by particular names depending on what phases are involved, as summarized in Table 1.2.1.

Table 1.2.1: 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 1.2.3 illustrates the relationships between the different ways matter can be classified.

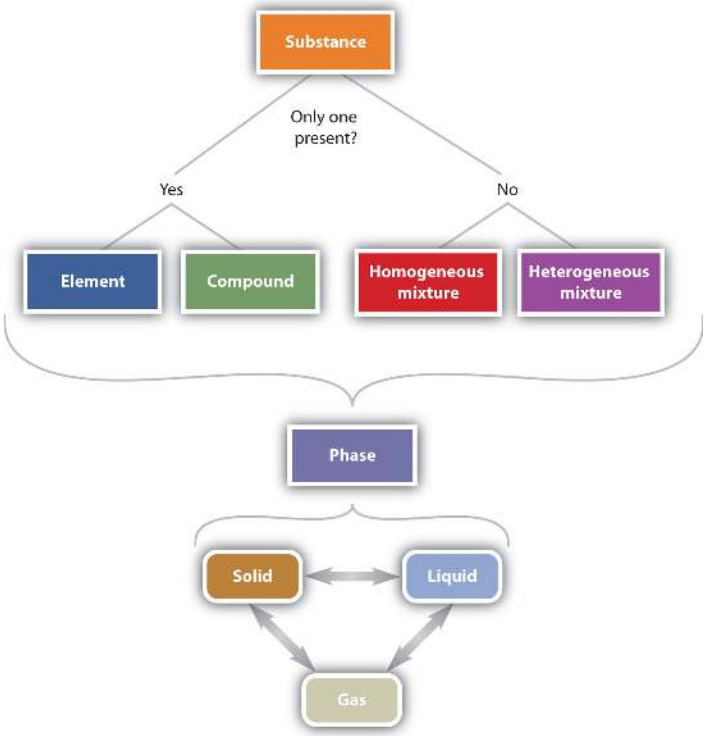


Figure 1.2.6: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.
This table starts with a substance. If there is only one present, it can either be an element or a compound. If there is more than one present, it can either be a homogeneous mixture or a heterogeneous mixture. From these choices, the substance can be in a certain phase. It can either be solid, liquid, or gas, and each phase can go from one to another.

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

Exercise 1.2.3

Does each statement refer to a chemical property or a physical property?

1. Balsa is a very light wood.
2. If held in a flame, magnesium metal burns in air.
3. Mercury has a density of 13.6 g/mL.
4. Human blood is red.

Answer

1. physical property
2. chemical property
3. physical property
4. physical property

Exercise 1.2.4

Does each statement refer to a chemical property or a physical property?

1. The elements sodium and chlorine can combine to make table salt.
2. The metal tungsten does not melt until its temperature exceeds 3,000°C.
3. The ingestion of ethyl alcohol can lead to disorientation and confusion.
4. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water

Answer

1. chemical property
2. physical property
3. chemical property
4. physical property

Exercise 1.2.5

Define *element*. How does it differ from a compound?

Answer

An element is a substance that cannot be broken down into chemically simpler components. Compounds can be broken down into simpler substances.

Exercise 1.2.6

Define *compound*. How does it differ from an element?

Answer

A compound is composed of two or more elements combined in a fixed ratio. An element is the simplest chemical substance.

Exercise 1.2.7

Give two examples of a heterogeneous mixture.

Answer

a salt and pepper mix and a bowl of cereal (answers will vary)

Exercise 1.2.8

Give two examples of a homogeneous mixture.

Answer

vinegar and rubbing alcohol (answers will vary)

Exercise 1.2.9

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

1. xenon, a substance that cannot be broken down into chemically simpler components
2. blood, a substance composed of several types of cells suspended in a salty solution called plasma
3. water, a substance composed of hydrogen and oxygen

Answer

1. element
2. heterogeneous mixture
3. compound

Exercise 1.2.10

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

1. sugar, a substance composed of carbon, hydrogen, and oxygen
2. hydrogen, the simplest chemical substance
3. dirt, a combination of rocks and decaying plant matter

Answer

1. compound
2. element
3. heterogeneous mixture

Exercise 1.2.11

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

1. air, primarily a mixture of nitrogen and oxygen
2. ringer's lactate, a standard fluid used in medicine that contains salt, potassium, and lactate compounds all dissolved in sterile water
3. tartaric acid, a substance composed of carbon, hydrogen, and oxygen

Answer

1. heterogeneous mixture
2. solution
3. compound

Exercise 1.2.12

What word describes each phase change?

1. solid to liquid
2. liquid to gas
3. solid to gas

Answer

1. melting or fusion
2. boiling or evaporation
3. sublimation

Exercise 1.2.13

1. What word describes each phase change?
    1. liquid to solid
    2. gas to liquid
    3. gas to solid

Answer

1. freezing
2. condensation
3. deposition

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1.3: 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 1.3.1); the nurse is also measuring.



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

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

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

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 1.3.1

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

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

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 1.3.2

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

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

Answer a

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

Answer b

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

Answer c

The number 32, and the unit is fluid ounces

Answer d

The number is 98.6, and the unit is degrees Fahrenheit

? Exercise 1.3.2

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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1.4: 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 1.4.1, 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:

$$K = °C + 273 \tag{1.4.1}$$

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 1.4.1: 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 1.4.1). 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 1.2×10^{-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 1.4.2. (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 1.4.2: 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 1.4.1: 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.

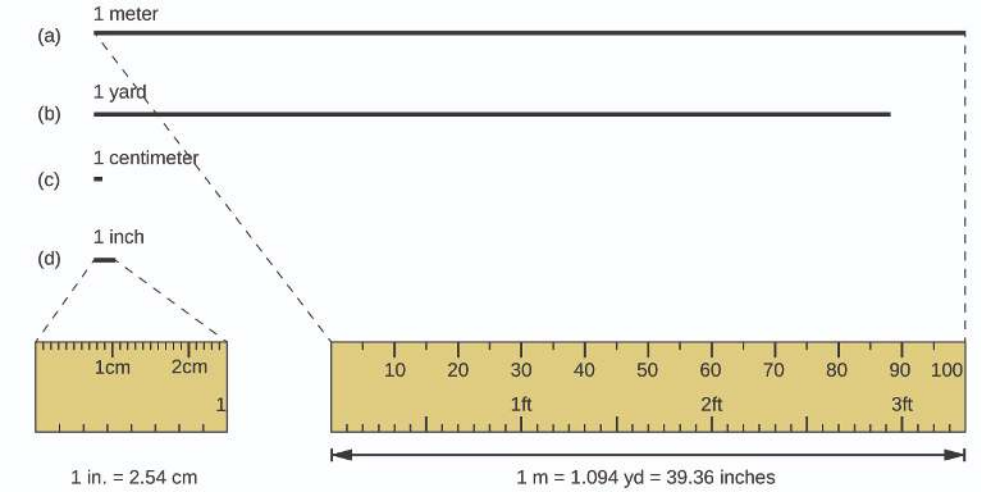


Figure 1.4.2: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

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 1.4.3, 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.

$$1\ mL = 1\ cm^3 \tag{1.4.2}$$

Example 1.4.1

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 1.4.1

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)

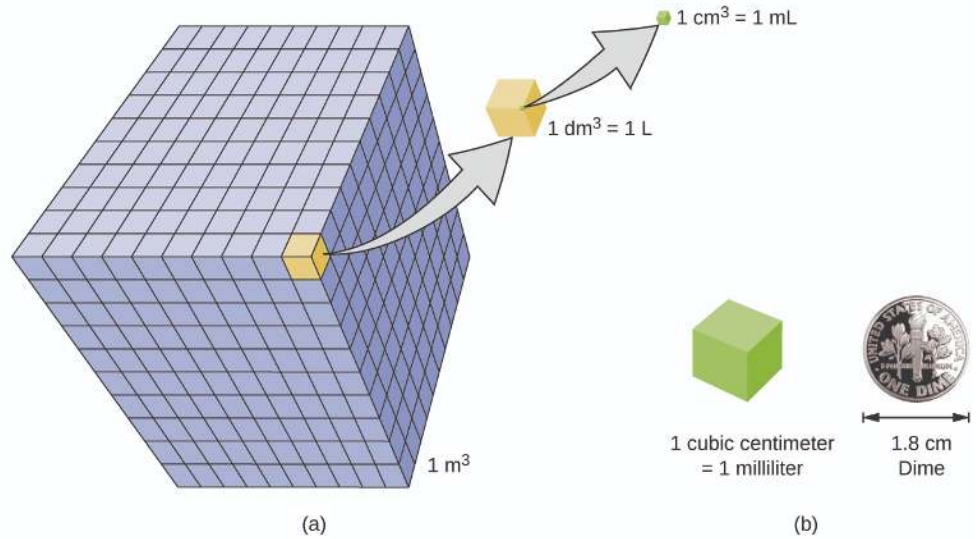


Figure 1.4.3: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a dime 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.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.4.3}$$

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 1.4.2: 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 1.4.2: 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 1.4.2: 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; $\text{mL} \times \frac{\text{g}}{\text{mL}} = \text{g}$ (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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1.5: Measurement Uncertainty, Accuracy, and Precision

Learning Objectives

By the end of this section, you will be able to:

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

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

Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

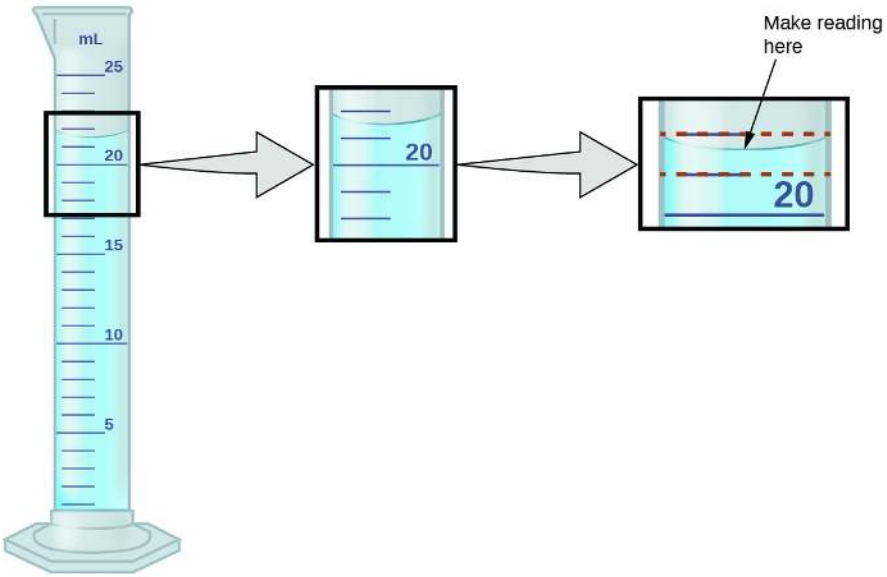
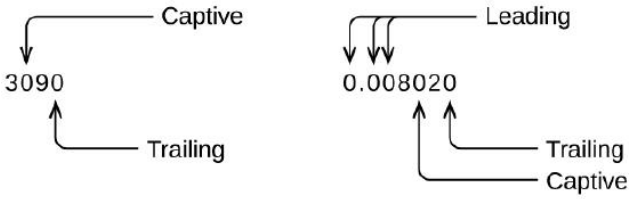


Figure 1.5.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in Figure 1.5.1. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

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

A measurement result is properly reported when its significant digits accurately represent the certainty of the measurement process. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms "leading," "trailing," and "captive" for the zeros and will consider how to deal with them.



Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.

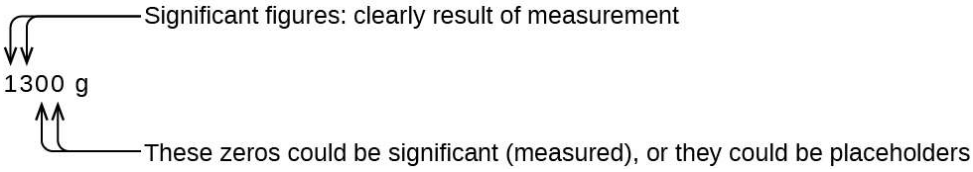


Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as 8.32407×10^{-3}; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.



When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely when evaluating whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as $3.17\ 10^8$ people.

Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. Take the uncertainty in measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for **rounding** numbers:

1. When adding or subtracting numbers, round the result to the same number of decimal places as the number with the least number of decimal places (the least certain value in terms of addition and subtraction).
2. When multiplying or dividing numbers, round the result to the same number of digits as the number with the least number of significant figures (the least certain value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, “round down” and leave the retained digit unchanged; if it is more than 5, “round up” and increase the retained digit by 1. If the dropped digit is 5, and it’s either the last digit in the number or it’s followed only by zeros, round up or down, whichever yields an even value for the retained digit. If any nonzero digits follow the dropped 5, round up. (The last part of this rule may strike you as a bit odd, but it’s based on reliable statistics and is aimed at avoiding any bias when dropping the digit “5,” since it is equally close to both possible values of the retained digit.)

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds “up” to 0.0287 (the dropped digit, 7, is greater than 5)
- 18.3384 rounds “down” to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds “up” to 6.88 (the dropped digit is 5, and a nonzero digit follows it)
- 92.85 rounds “down” to 92.8 (the dropped digit is 5, and the retained digit is even)

Let’s work through these rules with a few examples.

✔ Example 1.5.1: Rounding Numbers

Round the following to the indicated number of significant figures:

a. 31.57 (to two significant figures)
b. 8.1649 (to three significant figures)
c. 0.051065 (to four significant figures)
d. 0.90275 (to four significant figures)

Solution

a. 31.57 rounds “up” to 32 (the dropped digit is 5, and the retained digit is even)
b. 8.1649 rounds “down” to 8.16 (the dropped digit, 4, is less than 5)
c. 0.051065 rounds “down” to 0.05106 (the dropped digit is 5, and the retained digit is even)
d. 0.90275 rounds “up” to 0.9028 (the dropped digit is 5, and the retained digit is even)

Exercise 1.5.1

Round the following to the indicated number of significant figures:

a. 0.424 (to two significant figures)
b. 0.0038661 (to three significant figures)
c. 421.25 (to four significant figures)
d. 28,683.5 (to five significant figures)

Answer

a. 0.42
b. 0.00387
c. 421.2
d. 28,684

Example 1.5.2: Addition and Subtraction with Significant Figures

Rule: When adding or subtracting numbers, round the result to the same number of decimal places as the number with the fewest decimal places (i.e., the least certain value in terms of addition and subtraction).

a. Add 1.0023 g and 4.383 g.
b. Subtract 421.23 g from 486 g.

Solution

(a)

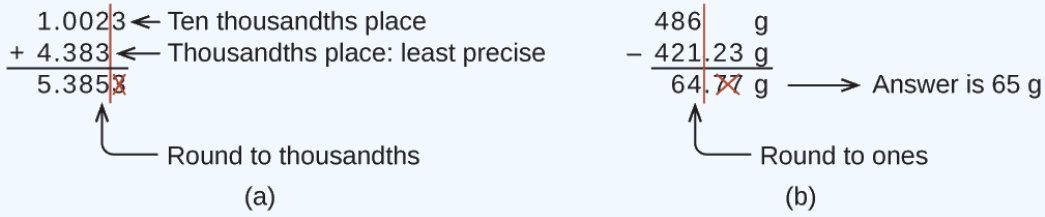
$$\begin{array}{r} 1.0023\,\text{g} \\ +\ \ 4.383\,\text{g} \\ \hline 5.3853\,\text{g} \end{array}$$

Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)

$$\begin{array}{r} 486\,\text{g} \\ -\ \ 421.23\,\text{g} \\ \hline 64.77\,\text{g} \end{array}$$

Answer is 65 g (round to the ones place; no decimal places)



Exercise 1.5.2

a. Add 2.334 mL and 0.31 mL.
b. Subtract 55.8752 m from 56.533 m.

Answer

a. 2.64 mL
b. 0.658 m

Example 1.5.3: Multiplication and Division with Significant Figures

Rule: When multiplying or dividing numbers, round the result to the same number of digits as the number with the fewest significant figures (the least certain value in terms of multiplication and division).

a. Multiply 0.6238 cm by 6.6 cm.
b. Divide 421.23 g by 486 mL.

Solution

(a)

$$\underbrace{0.6238\,\text{cm}}_{\text{four significant figures}} \times \underbrace{6.6\,\text{cm}}_{\text{two significant figures}} = 4.11708\,\text{cm}^2 \rightarrow \underbrace{4.1\,\text{cm}^2}_{\text{round to two significant figures}}$$

(b)

$$\underbrace{421.23\,\text{g}}_{\text{five significant figures}} \div \underbrace{486\,\text{mL}}_{\text{three significant figures}} = 0.866728\ldots\,\text{g/mL} \rightarrow \underbrace{0.867\,\text{g/mL}}_{\text{round to three significant figures}}$$

Exercise 1.5.3

a. Multiply 2.334 cm and 0.320 cm.
b. Divide 55.8752 m by 56.53 s.

Answer

a. 0.747 cm^2
b. 0.9884 m/s

In the midst of all these technicalities, it is important to keep in mind the reason for these rules about significant figures and rounding—to correctly represent the certainty of the values reported and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

Example 1.5.4: Calculation with Significant Figures

One common bathtub is 13.44 dm long, 5.920 dm wide, and 2.54 dm deep. Assume that the tub is rectangular and calculate its approximate volume in liters.

Solution

$$\begin{aligned} V &= l \times w \times d \\ &= 13.44\,\text{dm} \times 5.920\,\text{dm} \times 2.54\,\text{dm} \\ &= 202.09459\ldots\,\text{dm}^3 \text{ (value from calculator)} \\ &= 202\,\text{dm}^3 \text{ or } 202\,\text{L} \text{ (answer rounded to three significant figures)} \end{aligned}$$

Exercise 1.5.4

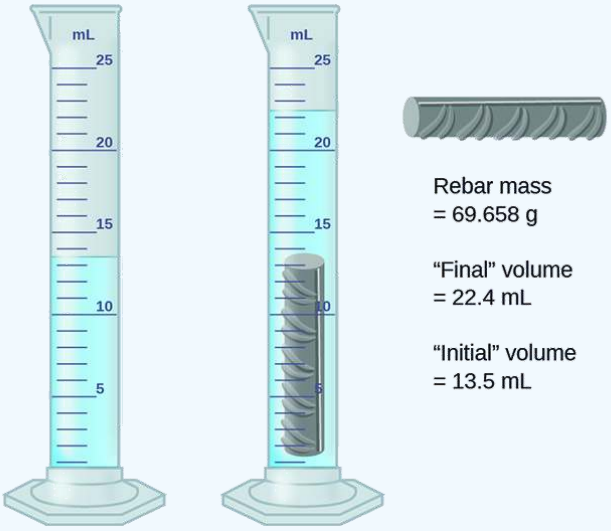
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

Example 1.5.5: Experimental Determination of Density Using Water Displacement

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.



a. Use these values to determine the density of this piece of rebar.
b. Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

The volume of the piece of rebar is equal to the volume of the water displaced:

$$\text{volume } = 22.4\,\text{mL} - 13.5\,\text{mL} = 8.9\,\text{mL} = 8.9\,\text{cm}^3$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)

The density is the mass-to-volume ratio:

$$\text{density } = \frac{\text{mass}}{\text{volume}} = \frac{69.658\,\text{g}}{8.9\,\text{cm}^3} = 7.8\,\text{g/cm}^3$$

(rounded to two significant figures, per the rule for multiplication and division)

The density of iron is 7.9 g/cm^3, very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

? Exercise 1.5.5

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.



a. Use these values to determine the density of this material.
b. Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Answer

19 g/cm^3

It is likely gold; the right appearance for gold and very close to the known density of gold at $19.3\,\mathrm{g/cm^3}$

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to evaluate both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 1.5.2).

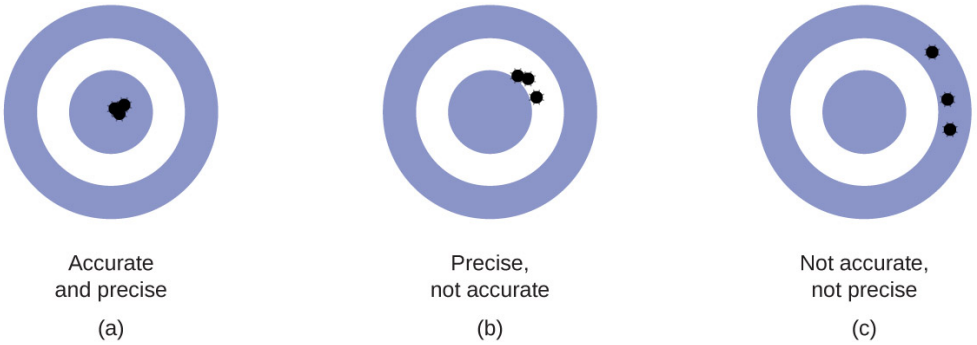


Figure 1.5.2: (a) These arrows are close to both the bull’s eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 1.5.1.

Table 1.5.1: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

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

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

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1.6: 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 1.5×10^6. The distance of the spacecraft from Mars can therefore be expressed as 1.5×10^6 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 1.6.1: 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 6.7×10^{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 1.689×10^3.

Answer c

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

? Exercise 1.6.1

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 1.492×10^3.

Answer b

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

Answer c

Moving the decimal point 5 places to the left yields 1.01325×10^5.

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 1.6.2

Express each number in standard, or conventional notation.

a. 5.27×10^4
b. 1.0008×10^6

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 1.6.2

Express each number in standard, or conventional notation.

a. 6.98×10^8
b. 1.005×10^2

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 6×10^{-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 1.6.3

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 6.567×10^{-6}.

Answer b

Move the decimal point four places to the right to get -4.004×10^{-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 1.23×10^{-13}.

Exercise 1.6.3

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 3.55×10^{-4}.

Answer b

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

Answer c

Moving the decimal point one place to the right gives -5.1204×10^{-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 1.6.4

Change the number in scientific notation to standard form.

a. 6.22×10^{-2}
b. 9.9×10^{-9}

Answer a

0.0622

Answer b

0.0000000099

Exercise 1.6.4

Change the number in scientific notation to standard form.

a. 9.98×10^{-5}
b. 5.109×10^{-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 1.6.1

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 1.6.2

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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1.7: 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:

$$\frac{3.55}{1} \times \frac{100 \text{ cm}}{1} = 355 \text{ cm} \tag{1.7.1}$$

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 1.7.1), 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 1.7.1 shows a **concept map** for constructing a proper conversion.

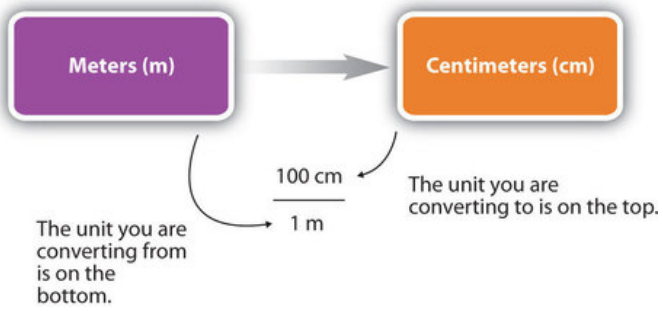


Figure 1.7.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Meters converted to centimeters. A fraction showing 100 cm over 1 m. The unit you convert to is on top, and the unit you convert from is on bottom.

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 1.7.1

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.



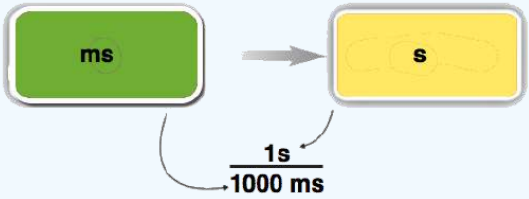
$$4.7 \cancel{\text{L}} \times \frac{1,000 \text{ mL}}{1 \cancel{\text{L}}} = 4,700 \text{ mL}$$

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

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

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

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



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

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

? Exercise 1.7.1

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 1.7.2: 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.

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

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

We have limited the final answer to three significant figures.

Exercise 1.7.2

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

Answer

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

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 m:

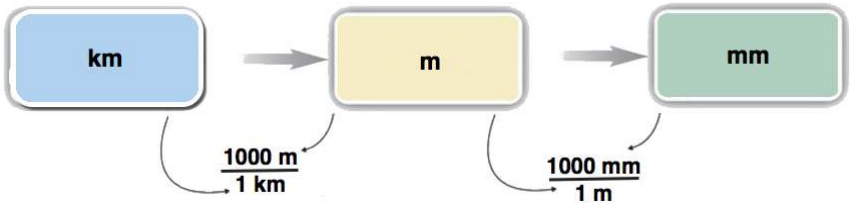
$$54,700 \cancel{\text{ m}} \times \frac{1,000 \text{ mm}}{1 \cancel{\text{ m}}} = 54,700,000 \text{ mm}$$

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

We have expressed the final answer in scientific notation.

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

Concept Map



Calculation

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

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

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

Either method—one step at a time or all the steps together—is acceptable. If you do all the steps together, the restriction for the proper number of significant figures should be done after the last step. As long as the math is performed correctly, you should get

the same answer no matter which method you use.

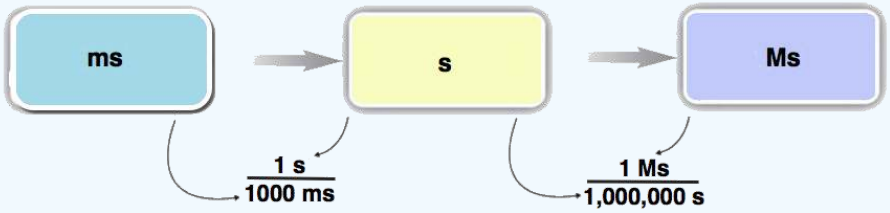
Example 1.7.3

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 1.7.3

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 1.0×10^{12} *nano*liters (nL) to *kilo*liters (kL).

Answers

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



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

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1.8: 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 1.8.1

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 1.8.1

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 1.8.2

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 1.8.2

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

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

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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.E: Chemistry, Matter, and Measurement (Exercises)

1. Does each statement refer to a chemical property or a physical property?

    a. Balsa is a very light wood.
    b. If held in a flame, magnesium metal burns in air.
    c. Mercury has a density of 13.6 g/mL.
    d. Human blood is red.

2. Does each statement refer to a chemical property or a physical property?

    a. The elements sodium and chlorine can combine to make table salt.
    b. The metal tungsten does not melt until its temperature exceeds 3,000°C.
    c. The ingestion of ethyl alcohol can lead to disorientation and confusion.
    d. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water.

3. Define *element*. How does it differ from a compound?

4. Define *compound*. How does it differ from an element?

5. Give two examples of a heterogeneous mixture.

6. Give two examples of a homogeneous mixture.

7. Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

    a. xenon, a substance that cannot be broken down into chemically simpler components
    b. blood, a substance composed of several types of cells suspended in a salty solution called plasma
    c. water, a substance composed of hydrogen and oxygen

8. Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

    a. sugar, a substance composed of carbon, hydrogen, and oxygen
    b. hydrogen, the simplest chemical substance
    c. dirt, a combination of rocks and decaying plant matter

9. Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.

    a. air, primarily a mixture of nitrogen and oxygen
    b. ringer's lactate, a standard fluid used in medicine that contains salt, potassium, and lactate compounds all dissolved in sterile water
    c. tartaric acid, a substance composed of carbon, hydrogen, and oxygen

10. Identify each material as an element, a compound, a heterogeneous mixture, or a solution.

    a. equal portions of salt and sand placed in a beaker and shaken up
    b. a combination of beeswax dissolved in liquid hexane
    c. hydrogen peroxide, a substance composed of hydrogen and oxygen

11. What word describes each phase change?

    a. solid to liquid
    b. liquid to gas
    c. solid to gas

12. What word describes each phase change?

    a. liquid to solid
    b. gas to liquid
    c. gas to solid

Answers

1.

a. physical property
b. chemical property
c. physical property
d. physical property

2.

a. chemical property
b. physical property
c. chemical property
d. physical property

3. An element is a substance that cannot be broken down into chemically simpler components. Compounds can be broken down into simpler substances.

4. A compound is composed of two or more elements combined in a fixed ratio. An element is the simplest chemical substance.

5. a salt and pepper mix and a bowl of cereal (answers will vary)

6. vinegar and rubbing alcohol (answers will vary)

7.

a. element
b. heterogeneous mixture
c. compound

8.

a. compound
b. element
c. heterogeneous mixture

9.

a. solution
b. solution
c. compound

10.

a. heterogeneous mixture
b. solution
c. compound

11.

a. melting or fusion
b. boiling or evaporation
c. sublimation

12.

a. freezing
b. condensation
c. deposition

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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: 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.

2.0: Prelude to Elements, Atoms, and the Periodic Table
2.1: Chemical Elements and Symbols
2.2: The Periodic Table
2.3: Early Ideas in Atomic Theory
2.4: Evolution of Atomic Theory
2.5: Atomic Structure and Symbolism
2.6: Electronic Structure of Atoms
2.7: Electron Configurations
2.8: Electron Configurations and the Periodic Table
2.9: Periodic Trends
2.E: Elements, Atoms, and the Periodic Table (Exercises)
2.S: Elements, Atoms, and the Periodic Table (Summary)

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2.0: 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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2.1: Chemical Elements and Symbols

Learning Objectives

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

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



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

Elemental Names and Symbols

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

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

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table 2.1.1 lists the names and symbols of some of the most familiar elements.

Table 2.1.1: Element Names and Symbols

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

*The symbol comes from the Latin name of element. †The symbol for tungsten comes from its German name—*wolfram*.

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

Elements in Nature and the Human Body

The elements vary widely in abundance. In the universe as a whole, the most common element is hydrogen (about 90% of atoms), followed by helium (most of the remaining 10%). All other elements are present in relatively minuscule amounts, as far as we can detect. On the planet Earth, however, the situation is rather different (Table 2.1.2). Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen, the most abundant element in the universe, makes up only 0.14% of Earth's crust.

Table 2.1.2: Elemental Composition of Earth and the Human Body

Earth's Crust		Human Body	
Element	**Percentage**	**Element**	**Percentage**
oxygen	46.1	oxygen	61
silicon	28.2	carbon	23
aluminum	8.23	hydrogen	10
iron	5.53	nitrogen	2.6
calcium	4.15	calcium	1.4
sodium	2.36	phosphorus	1.1
magnesium	2.33	sulfur	0.20
potassium	2.09	potassium	0.20
titanium	0.565	sodium	0.14
hydrogen	0.14	chlorine	0.12
phosphorus	0.105	magnesium	0.027
all others	0.174	silicon	0.026

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

Table 2.1.2 also lists the relative abundances of elements in the human body. If you compare both compositions, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry; carbon is part of the 0.174% representing "other" elements.

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

Looking Closer: The Phosphorous Bottleneck

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

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



Figure 2.1.2: The eutrophication of the Potomac River is evident from the bright green water, caused by a dense bloom of cyanobacteria. (CC BY-SA 3.0; Alexandr Trubetskoy via Wikipedia)

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

Example 2.1.1

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

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

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

Solution

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

Exercise 2.1.1

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

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

Answer a

Mn

Answer b

Mg

Answer c

Ne

Answer d

N

Answer e

Ag

Example 2.1.2

What element is represented by each chemical symbol?

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

a. sodium
b.
c. mercury
d.
e. phosphorus
f.
g. potassium
h. iodine
i.

Exercise 2.1.2

What element is represented by each chemical symbol?

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

Answer a

lead

Answer b

tin

Answer c

uranium

Answer d

oxygen

Answer e

fluorine

Chemical Formulas

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

$$\underbrace{\mathrm{H_2O}}_{\substack{2\text{ H atoms}\\1\text{ O atom}}} \quad \underbrace{\mathrm{H_2SO_4}}_{\substack{2\text{ H atoms}\\1\text{ S atom}\\4\text{ O atoms}}} \quad \underbrace{\mathrm{C_{12}H_{22}O_{11}}}_{\substack{12\text{ H atoms}\\22\text{ C atoms}\\11\text{ O atoms}}} \tag{2.1.1}$$

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

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

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

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

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

and decomposing this to elements gives

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

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

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

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

? Exercise 2.1.3

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

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

Answer a

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

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

Answer b

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

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

Answer c

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

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

Answer d

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

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

Key Takeaways

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

Contributors and Attributions

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2.2: The Periodic Table

Learning Objectives

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

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

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

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

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

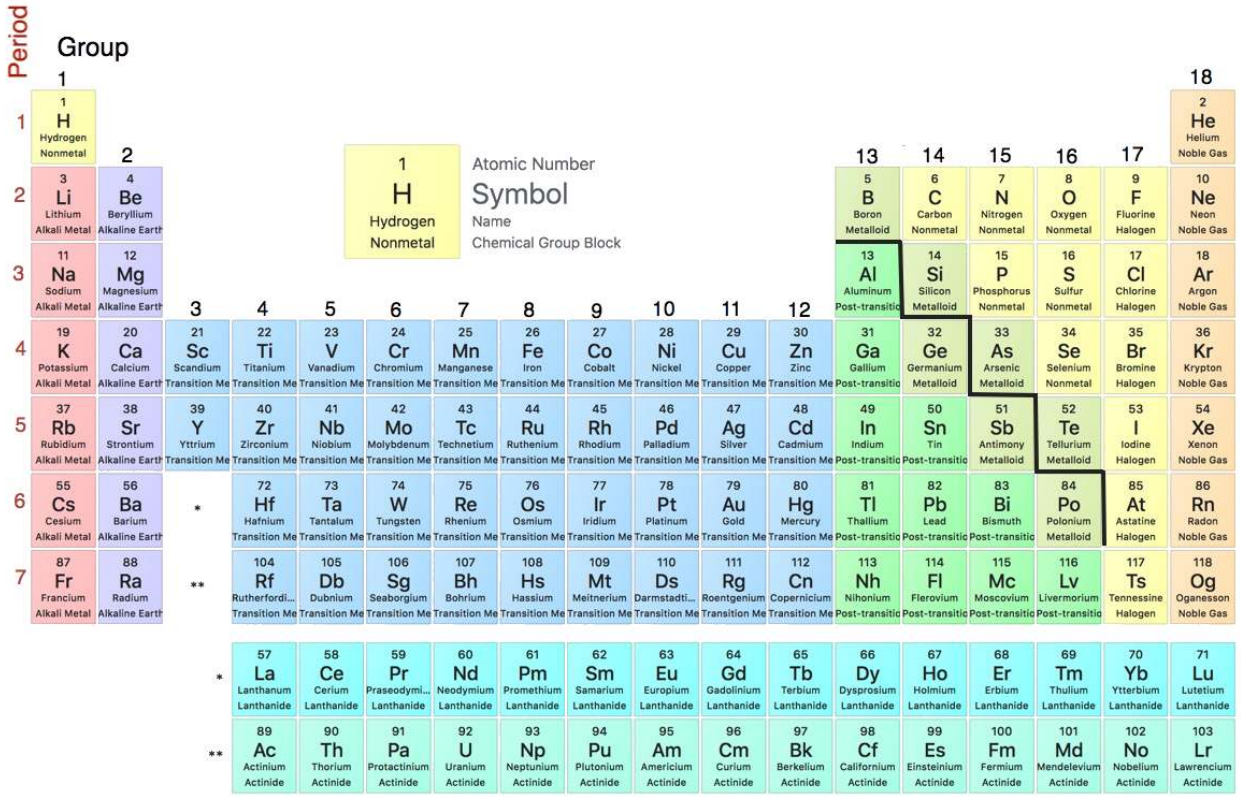


Figure 2.2.1: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares). An interactive Periodic table can be found here.

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

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

Metals, Nonmetals, and Metalloids

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

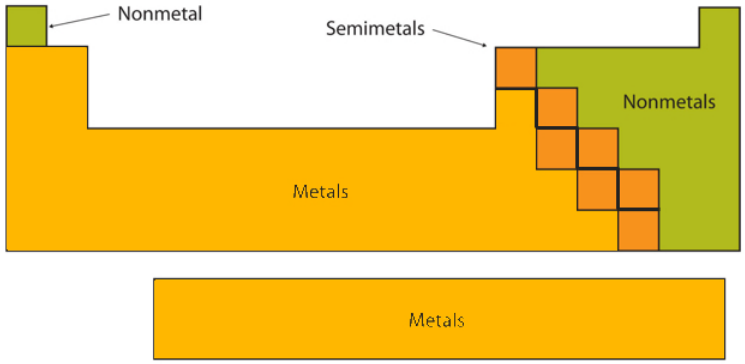


Figure 2.2.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 2.2.1

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

a. Se
b. Mg
c. Ge

Solution

a. The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.2.2, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be a metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

Exercise 2.2.1

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

Answer

metal

Representative, Transition, and Inner-transition

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

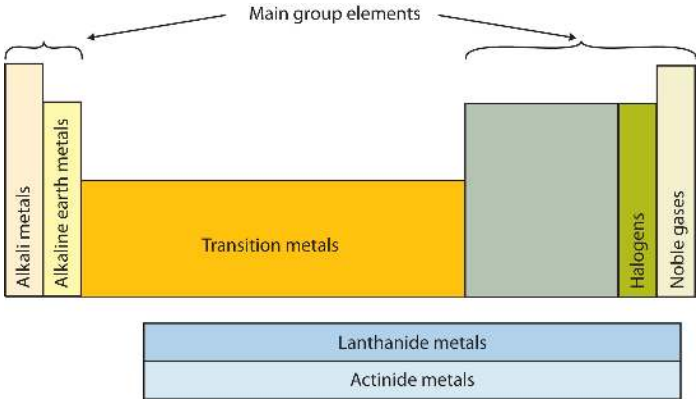


Figure 2.2.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

To Your Health: Transition Metals in the Body

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

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

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

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

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

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2.3: Early Ideas in Atomic Theory

Learning Objectives

By the end of this section, you will be able to:

- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for "indivisible." They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four "elements"—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and "elements" as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of Dalton's atomic theory.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure 2.3.1). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

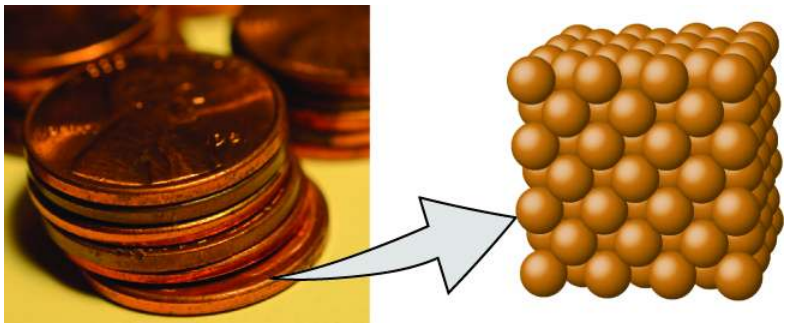


Figure 2.3.1: A pre-1982 copper penny (left) contains approximately 3 10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure 2.3.2).

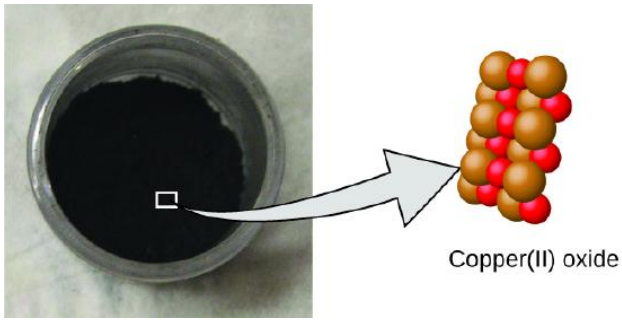


Figure 2.3.2: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure 2.3.3).

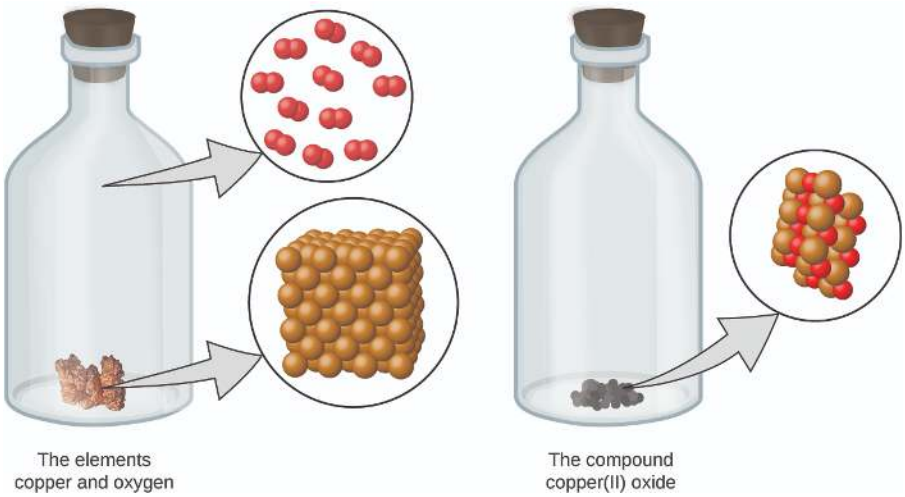
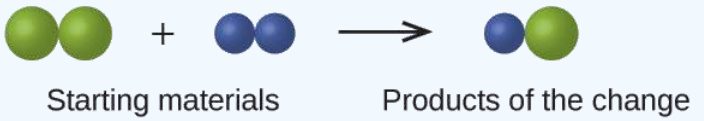


Figure 2.3.3: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by http://images-of-elements.com/copper.php)

Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

✔ Example 2.3.1: Testing Dalton's Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

? Exercise 2.3.1

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



Answer

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 2.1.

Table 2.1: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	
B	22.33 g	4.19 g	
C	19.40 g	3.64 g	

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The law of multiple proportions states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure 2.3.4).

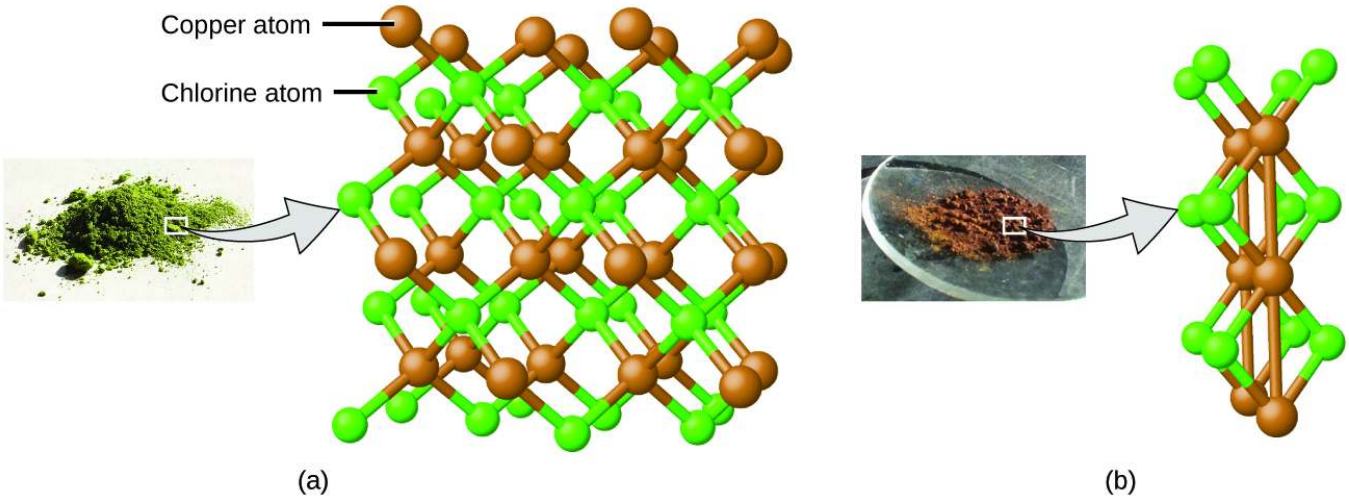


Figure 2.3.4: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)

Example 2.3.2: Laws of Definite and Multiple Proportions

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of oxygen to carbon is:

In compound B, the mass ratio of oxygen to carbon is:

The ratio of these ratios is:

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much oxygen per amount of carbon (or twice as much carbon per amount of oxygen) as B. A possible pair of compounds that would fit this relationship would be A = CO and B = CO_2.

Exercise 2.3.1

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Answer

In compound X, the mass ratio of carbon to hydrogen is In compound Y, the mass ratio of carbon to hydrogen is The ratio of these ratios is This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

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2.4: Evolution of Atomic Theory

Learning Objectives

By the end of this section, you will be able to:

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Define isotopes and give examples for several elements

If matter is composed of atoms, what are atoms composed of? Are they the smallest particles, or is there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure 2.4.1).

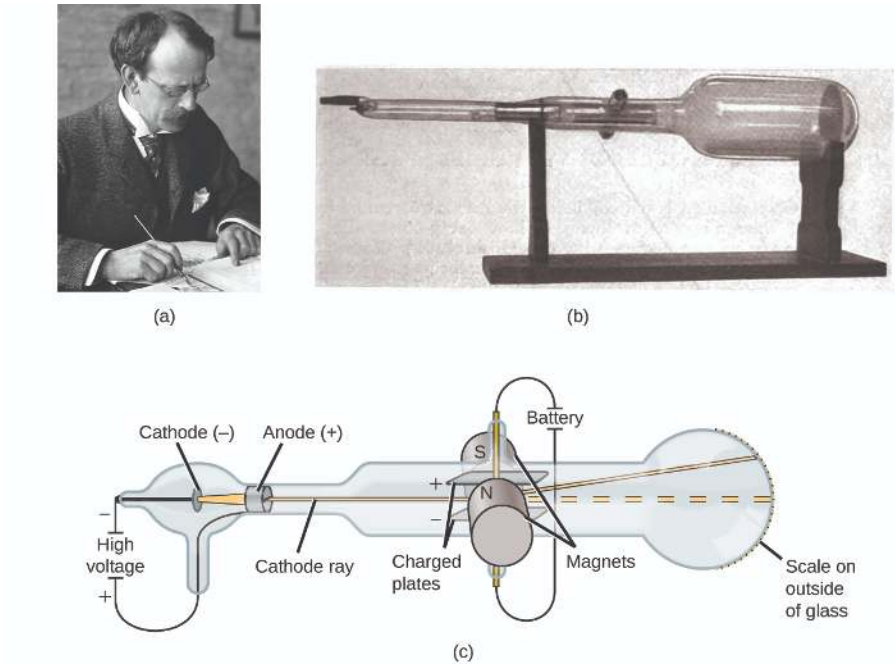


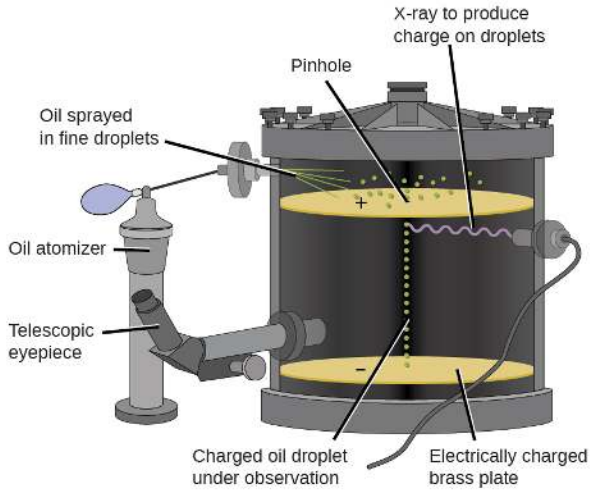
Figure 2.4.1: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons)

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we now call an electron, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term "electron" was coined in 1891 by Irish physicist George Stoney, from "*electr*ic i*on*."

Link to Learning

Click here to hear Thomson describe his discovery in his own voice.

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his “oil drop” experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 2.4.2).



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

Figure 2.4.2: Millikan’s experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6 10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6 10^{-19} C), two electrons (2 times 1.6 10^{-19} C), three electrons (3 times 1.6 10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan’s research, and the charge-to-mass ratio was already known due to Thomson’s research (1.759 10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the “plum pudding” model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure 2.4.3).

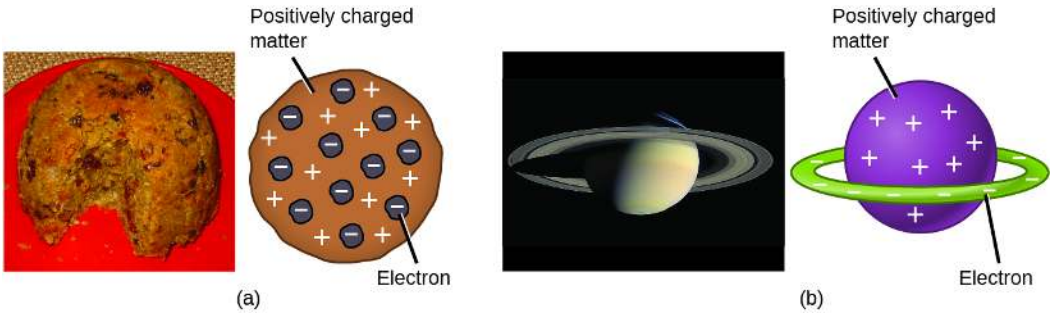


Figure 2.4.3: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” (credit a: modification of work by “Man vyi”/Wikimedia Commons; credit b: modification of work by “NASA”/Wikimedia Commons)

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

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure 2.4.4). Rutherford described finding these results: “It was quite the most incredible event that has ever happened to me in my life. 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.”[1]

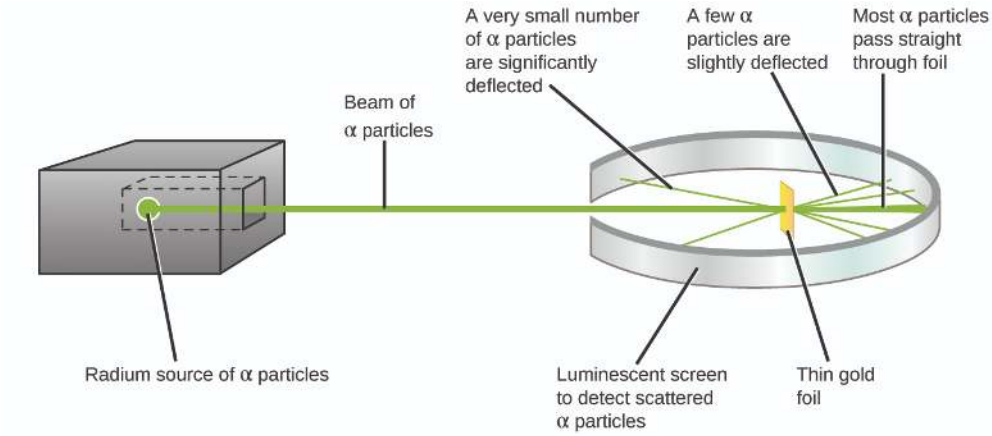


Figure 2.4.4: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the nucleus, must be at the center of each atom.

Link to Learning

View this simulation of the Rutherford gold foil experiment. Adjust the slit width to produce a narrower or broader beam of α particles to see how that affects the scattering pattern.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure 2.4.5). After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

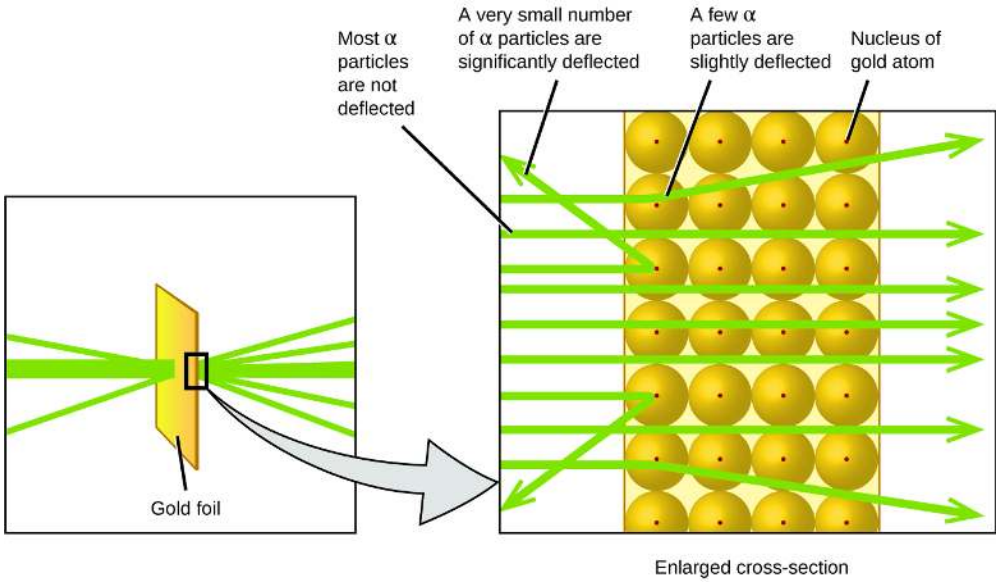


Figure 2.4.5: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

Link to Learning

The Rutherford Scattering simulation allows you to investigate the differences between a "plum pudding" atom and a Rutherford atom by firing α particles at each type of atom.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a "new element" produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called isotopes—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of neutrons, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this chapter.

Footnotes

- 1Ernest Rutherford, “The Development of the Theory of Atomic Structure,” ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/it...e032734mbp.pdf.

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2.5: Atomic Structure and Symbolism

Learning Objectives

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure 2.5.1).



Figure 2.5.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber).

The diagram on the left shows a picture of an atom with a nucleus. The central figure shows a photograph of an American football stadium. The figure on the right shows a photograph of a handful of blueberries.

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the atomic mass unit (amu) and the fundamental unit of charge (e). The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12" as will be discussed later in this module.) Thus, one amu is exactly $1/12$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The Dalton (Da) and the unified atomic mass unit (u) are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton. The properties of these fundamental particles are summarized in Table 2.5.1. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than the 12.00 amu of an actual carbon-12 atom. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table 2.5.1: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

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

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

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

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

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an anion. Positively charged atoms called cations are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = 1+). A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2− charge (8 − 10 = 2−).

Example 2.5.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 2.5.2).



(a)



(b)

Figure 2.5.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

Figure A shows a photo of a person who has a very swollen thyroid in his or her neck. Figure B shows a photo of a canister of Morton iodized salt.

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

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

? Exercise 2.5.1

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

Answer

78 protons; 117 neutrons; charge is 4+

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 2.5.3). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



Figure 2.5.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. from Wikipedia (user: Materialscientist).

The symbols for several common elements and their atoms are listed in Table 2.5.2. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

Table 2.5.2: Some Common Elements and Their Symbols

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

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

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 2.5.4). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

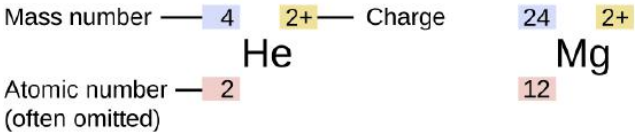


Figure 2.5.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

This diagram shows the symbol for helium, "H e." The number to the upper left of the symbol is the mass number, which is 4. The number to the upper right of the symbol is the charge which is positive 2. The number to the lower left of the symbol is the atomic number, which is 2. This number is often omitted. Also shown is "M g" which stands for magnesium It has a mass number of 24, a charge of positive 2, and an atomic number of 12.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 2.5.2. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table 2.5.2: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}\mathrm{H}$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}\mathrm{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}\mathrm{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}\mathrm{He}$	2	2	1	3.01603	0.00013
	$^{4}_{2}\mathrm{He}$	2	2	2	4.0026	100
lithium	$^{6}_{3}\mathrm{Li}$	3	3	3	6.0151	7.59
	$^{7}_{3}\mathrm{Li}$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}\mathrm{Be}$	4	4	5	9.0122	100
boron	$^{10}_{5}\mathrm{B}$	5	5	5	10.0129	19.9
	$^{11}_{5}\mathrm{B}$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}\mathrm{C}$	6	6	6	12.0000	98.89
	$^{13}_{6}\mathrm{C}$	6	6	7	13.0034	1.11
	$^{14}_{6}\mathrm{C}$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}\mathrm{N}$	7	7	7	14.0031	99.63
	$^{15}_{7}\mathrm{N}$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}\mathrm{O}$	8	8	8	15.9949	99.757
	$^{17}_{8}\mathrm{O}$	8	8	9	16.9991	0.038
	$^{18}_{8}\mathrm{O}$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}\mathrm{F}$	9	9	10	18.9984	100
neon	$^{20}_{10}\mathrm{Ne}$	10	10	10	19.9924	90.48
	$^{21}_{10}\mathrm{Ne}$	10	10	11	20.9938	0.27
	$^{22}_{10}\mathrm{Ne}$	10	10	12	21.9914	9.25

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the atomic mass of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\begin{aligned}\text{boron average mass} &= (0.199 \times 10.0129\ \text{amu}) + (0.801 \times 11.0093\ \text{amu}) \\ &= 1.99\ \text{amu} + 8.82\ \text{amu} \\ &= 10.81\ \text{amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Example 2.5.2: Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

$$\begin{aligned}\text{average mass} &= (0.9184 \times 19.9924\ \text{amu}) + (0.0047 \times 20.9940\ \text{amu}) + (0.0769 \times 21.9914\ \text{amu}) \\ &= (18.36 + 0.099 + 1.69)\ \text{amu} \\ &= 20.15\ \text{amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

Exercise 2.5.2

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Answer

24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

Example 2.5.3: Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl})$$

If we let x represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by $1.00 - x$.

(The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal 1.00 − the fraction of ^{35}Cl.)

Substituting this into the average mass equation, we have:

$$\begin{aligned}35.453\ \text{amu} &= (x \times 34.96885\ \text{amu}) + [(1.00 - x) \times 36.96590\ \text{amu}] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576\end{aligned}$$

So solving yields: $x = 0.7576$, which means that $1.00 - 0.7576 = 0.2424$. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl.

? Exercise 2.5.3

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Answer

69.15% Cu-63 and 30.85% Cu-65

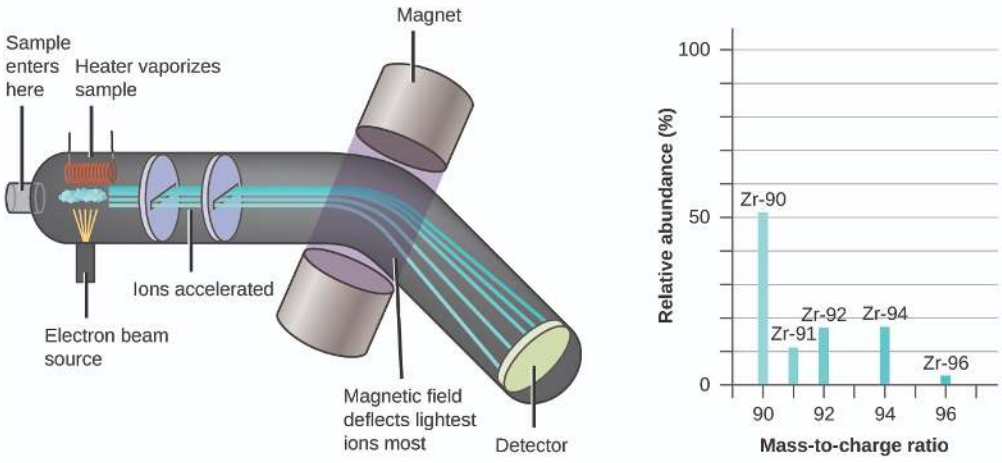
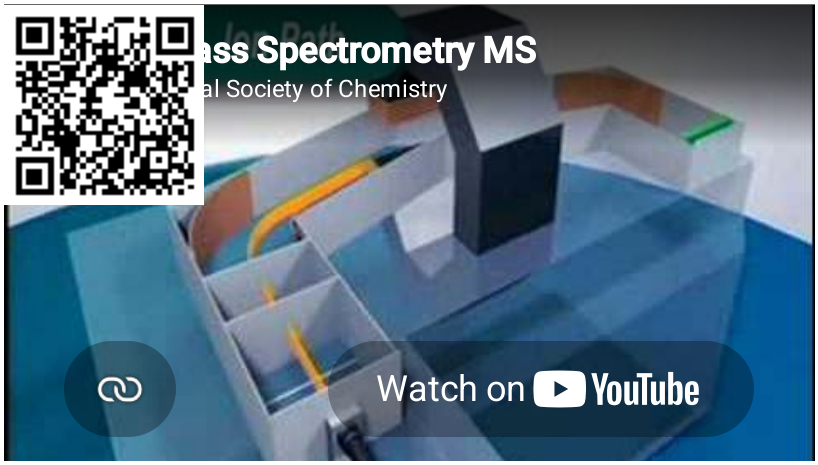


Figure 2.5.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

The left diagram shows how a mass spectrometer works. The graph to the right of the spectrometer shows a mass spectrum of zirconium. The relative abundance, as a percentage from 0 to 100, is graphed on the y axis, and the mass to charge ratio is graphed on the x axis. The sample contains five different isomers of zirconium.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 2.5.5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.



Video 2.5.1*: Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $1/12$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1− and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

Key Equations

- $\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$

Glossary

anion
negatively charged atom or molecule (contains more electrons than protons)

atomic mass
average mass of atoms of an element, expressed in amu

atomic mass unit (amu)
(also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

atomic number (Z)
number of protons in the nucleus of an atom

cation
positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol

one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)

alternative unit equivalent to the atomic mass unit

fundamental unit of charge

(also called the elementary charge) equals the magnitude of the charge of an electron (e) with $e = 1.602 \times 10^{-19}$ C

ion

electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)

sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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2.6: Electronic Structure of Atoms

Learning Objectives

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

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

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

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

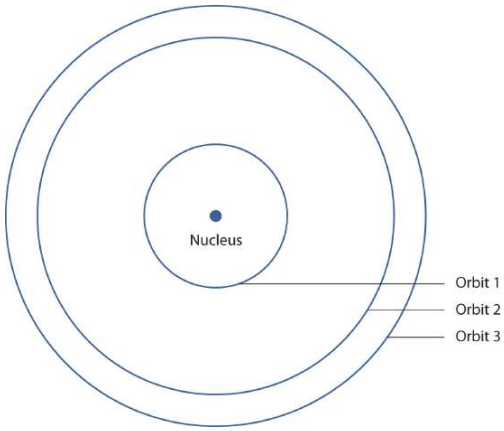


Figure 2.6.1: Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

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

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

Electron Arrangements: Shells, Subshells, and Orbitals

Electrons are organized according to their energies into sets called **shells** (labeled by the principle quantum number, ***n***). Generally the higher the energy of a shell, the farther it is (on average) from the nucleus. Shells do not have specific, fixed distances from the nucleus, but an electron in a higher-energy shell will spend more time farther from the nucleus than does an electron in a lower-energy shell.

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

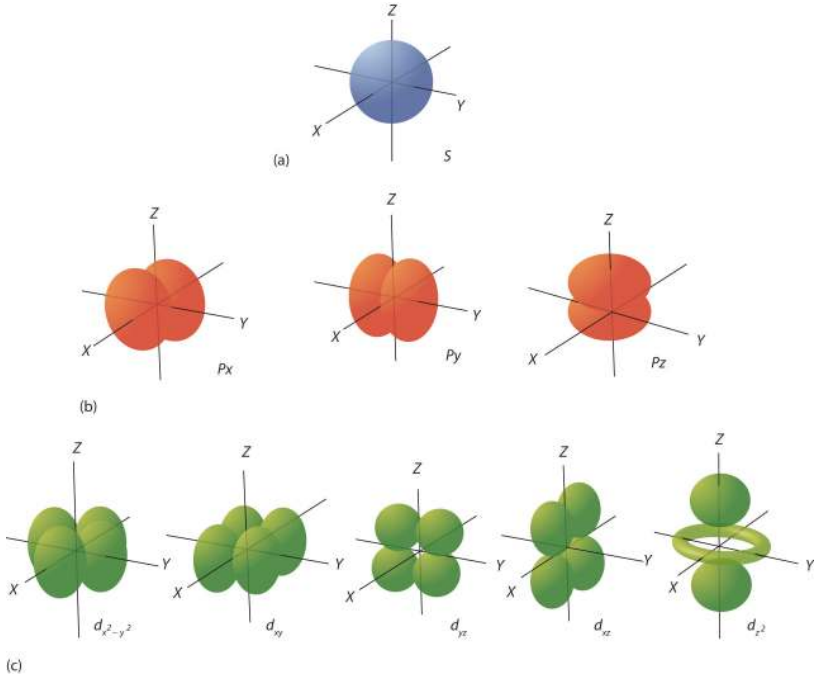


Figure 2.6.1: Electron Orbitals. (a) The lone *s* orbital in an *s* subshell is spherical in distribution. (b) The three *p* orbitals have two lobes, shaped kind of like dumbbells, each is oriented around the nucleus along a different axis. (c) The five *d* orbitals have four lobes, except for the d_{z^2}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

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

Table 2.6.1: Shells and Subshells

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

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

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2.7: Electron Configurations

Learning Objectives

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

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

We use numbers to indicate which shell an electron is in. The first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1*s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $\mathbf{1}s^{\mathbf{1}}$ (spoken as “one-ess-one”) to describe the electron arrangement or distribution of electrons in hydrogen. This structure is called an **electron configuration** and is unique to hydrogen.

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

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

The shell diagram for a lithium atom (Figure 2.7.1). The shell closest to the nucleus (first shell) has 2 dots representing the 2 electrons in **1*s***, while the outermost shell (**2*s***) has 1 electron.

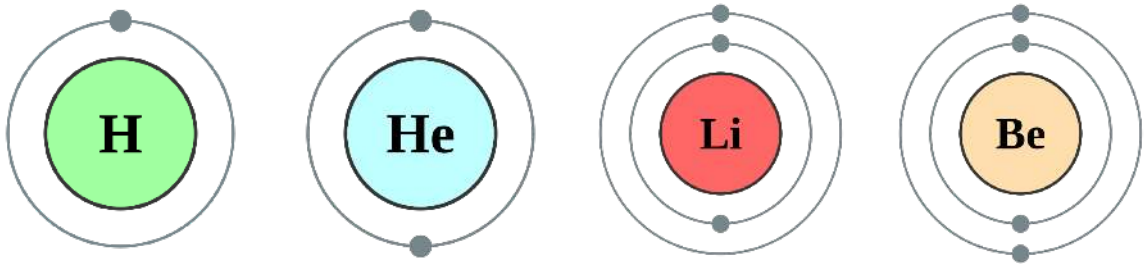


Figure 2.7.1: Shell diagrams of hydrogen (H), helium (He), lithium (Li), and Berryellium (Be) atoms. (CC BY-SA 2.0 UK; Greg Robson modified by Pumbaa via Wikipedia)

There are a set of general rules that are used to figure out the electron configuration of an atomic species: **Aufbau Principle**, **Hund's Rule** and the **Pauli-Exclusion Principle**.

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

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

six electrons. The next six elements progressively fill up the 2p subshell:

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

At the end of the period the element neon, has filled the 2*s*, and 2*p* subshells, which completes the second shell. Now atoms with more electrons now must begin the third shell starting with the 3*s* subshell. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^2 2s^2 2p^6 3s^2 3p^1$. However, a curious thing happens after the 3*p* subshell is filled: the 4*s* subshell begins to fill before the 3*d* subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms.

Table 2.7.1: Electron Configurations of the First 20 Elements

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

Noble Gas Configuration

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

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

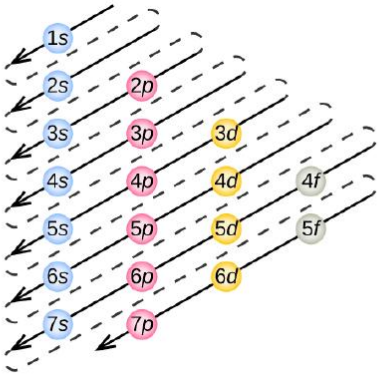


Figure 2.7.2: The order of electron filling in an atom. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

Example 2.7.1: Electronic Configuration of Phosphorus Atoms

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

Solution

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

Exercise 2.7.1: Electronic Configuration of Chlorine Atoms

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

Answer

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

Orbital Diagrams

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

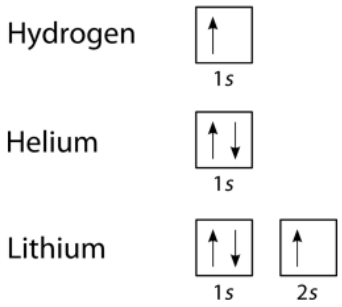


Figure 2.7.3: Orbital diagrams for hydrogen, helium, and lithium.

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

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

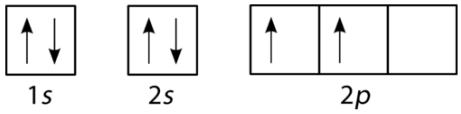


Figure 2.7.4: Orbital diagram for carbon.

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

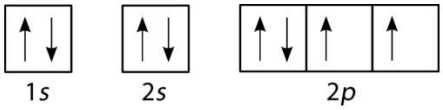


Figure 2.7.5: Orbital diagram for oxygen.

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

Example 2.7.3: Carbon Atoms

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

Solution

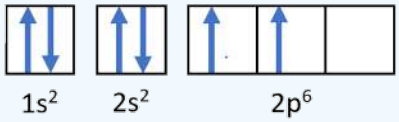
Step 1: List the known quantities and plan the problem.

Known

- Atomic number of carbon, Z=6

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

Step 2: Construct the diagram.



Orbital filling diagram for carbon.

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

Step 3: Think about your result.

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

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2.8: Electron Configurations and the Periodic Table

Learning Objectives

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

Remember, that the periodic table as a tool for organizing the known chemical elements(Figure 2.8.1). The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns. Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations: the shape of the periodic table mimics the filling of the subshells with electrons.

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

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the $n = 1$ shell is filled. These two elements make up the first row of the periodic table (Figure 2.8.1)

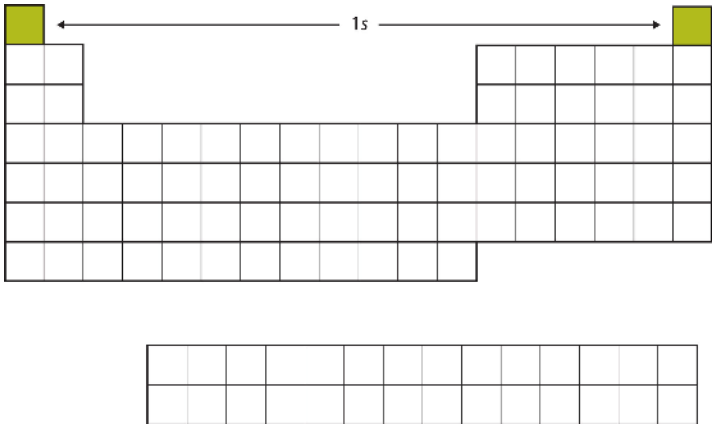


Figure 2.8.1: The 1*s* Subshell. H and He represent the filling of the 1*s* subshell.

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

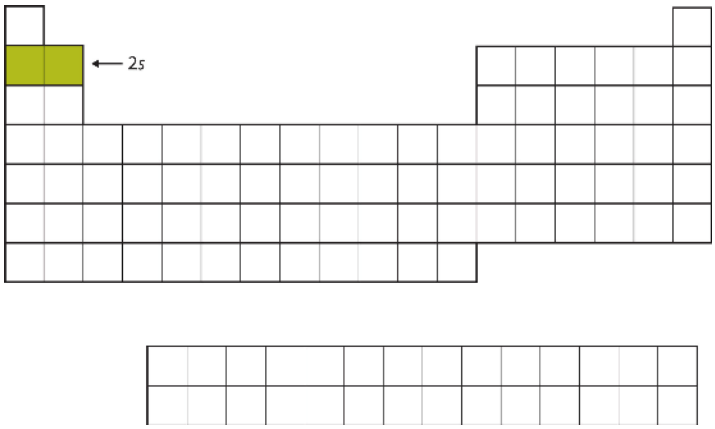


Figure 2.8.2: The 2*s* Subshell. In Li and Be, the 2*s* subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 2.8.3).

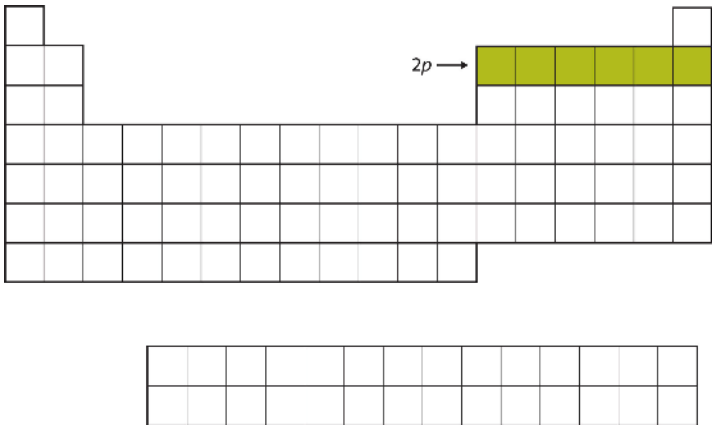


Figure 2.8.3: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 2.8.4).

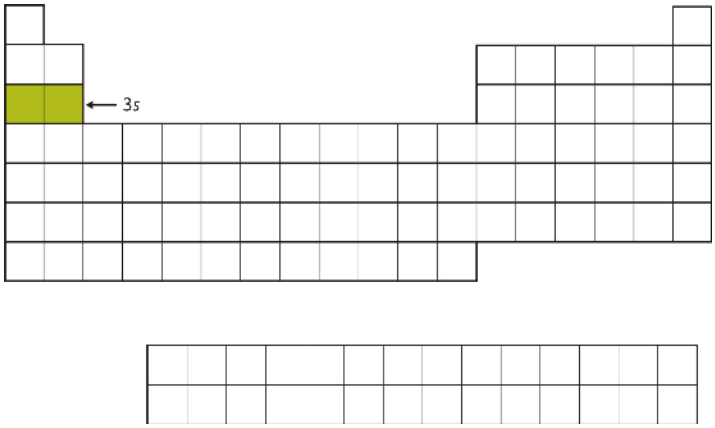


Figure 2.8.4: The 3*s* Subshell. Now the 3*s* subshell is being occupied.

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

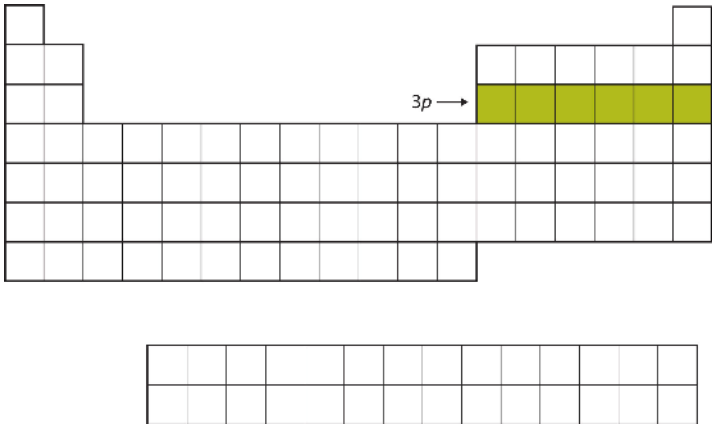


Figure 2.8.5: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

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

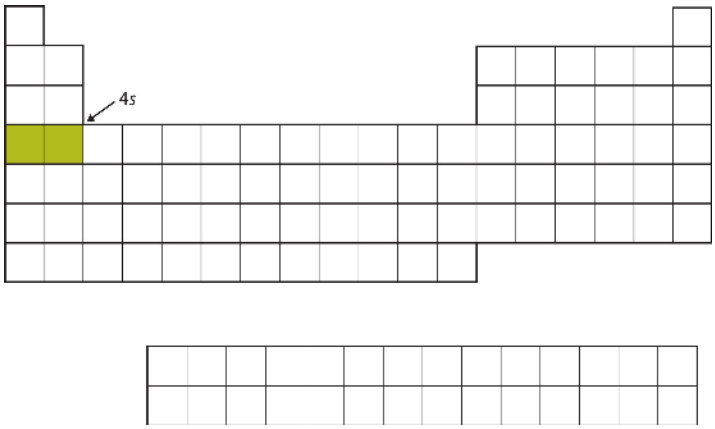


Figure 2.8.6: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure 2.8.7).

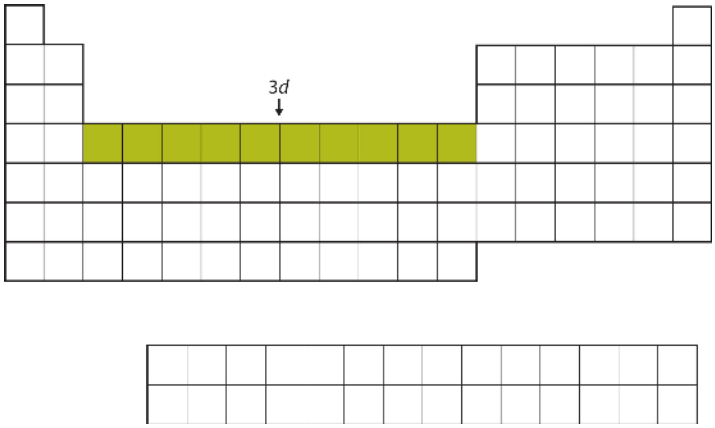


Figure 2.8.7: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

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

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** are the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 2.8.8 shows the blocks of the periodic table.

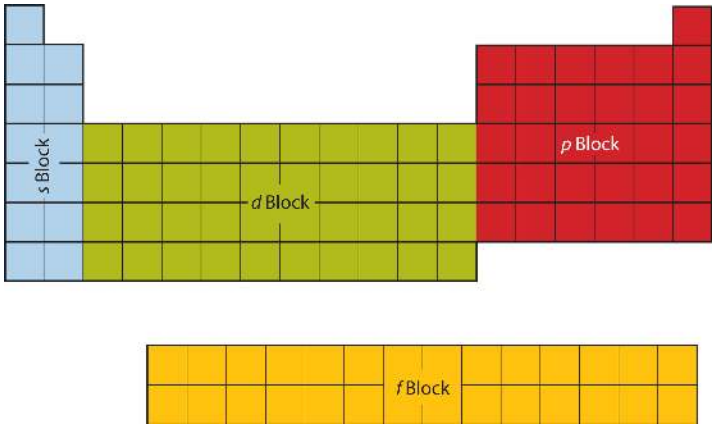


Figure 2.8.8: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

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

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

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

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

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

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 2.8.9. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^23d^{10}4p^4$, as expected.

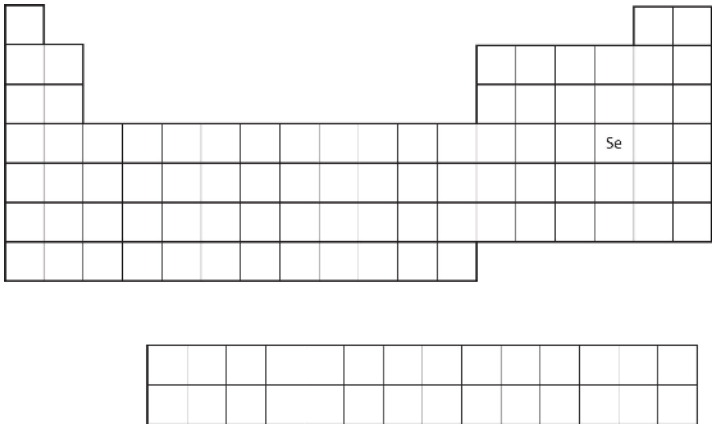


Figure 2.8.9: Selenium on the Periodic Table

Example 2.8.1

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

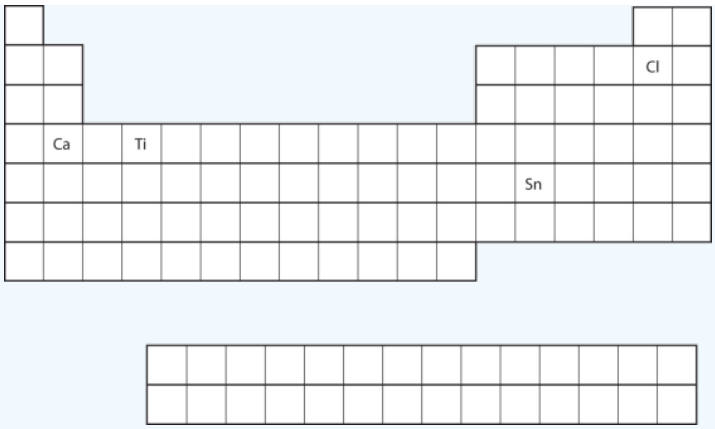


Figure 2.8.10: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

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

? Exercise 2.8.1

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

a. Ti
b. Cl

Answer a

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

Answer b

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

✓ Example 2.8.2: Aluminum

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

Solution

Aluminum has 13 electrons.

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

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

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

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

? Exercise 2.8.2

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

Answer

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

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

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

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

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

Summary

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

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2.9: Periodic Trends

Learning Objectives

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

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 2.9.4. 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.**

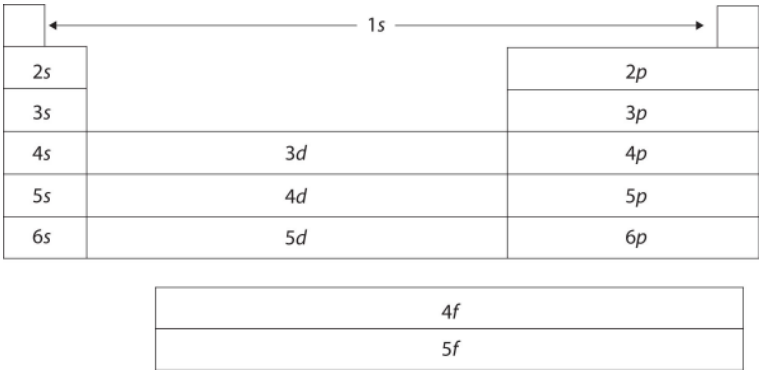


Figure 2.9.4 The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

Example 2.9.1

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

Exercise 2.9.1

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 2.9.1. 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
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*

** 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 2.9.5). 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 H_2 molecule is measured to be $74\ \text{pm}$. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = 37\ \text{pm}$.

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 2.9.5

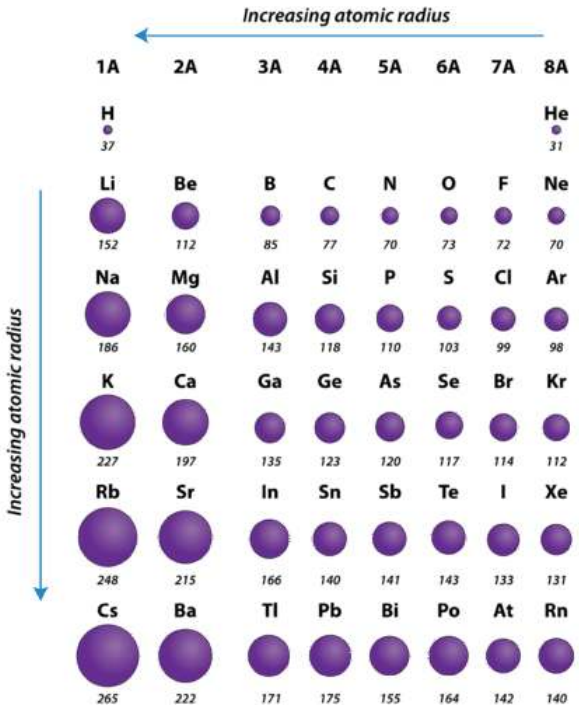


Figure 2.9.5 Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

✔ Example 2.9.2

Using the periodic table (rather than Figure 2.9.5), 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 2.9.2

Using the periodic table (rather than Figure 2.9.5), 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.

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.

2.7: The Periodic Table

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2.E: Elements, Atoms, and the Periodic Table (Exercises)

02.E: Exercises II

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2.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

3: 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.

3.0: Prelude to Ionic Bonding and Simple Ionic Compounds
3.1: Two Types of Bonding
3.2: Ions
3.3: Formulas of Ionic Compounds
3.4: Naming Ionic Compounds
3.5: Formula Mass
3.6: Some Properties of Ionic Compounds
3.E: Ionic Bonding and Simple Ionic Compounds (Exercises)
3.S: Ionic Bonding and Simple Ionic Compounds (Summary)

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3.0: 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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3.1: 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 3.1.1

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:

Table explaining the solution to the example.

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

Exercise 3.1.1

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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3.2: 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.

$$\text{Na: } 1s^2 2s^2 2p^6 3s^1$$

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.

$$\begin{array}{ccc} \text{Na} & \rightarrow & \text{Na}^+ + \text{e}^- \\ 1s^2\ 2s^2\ 2p^6\ 3s^1 & & 1s^2\ 2s^2\ 2p^6 \text{ (octet)} \end{array}$$

Figure 3.2.1 is a graphical depiction of this process.

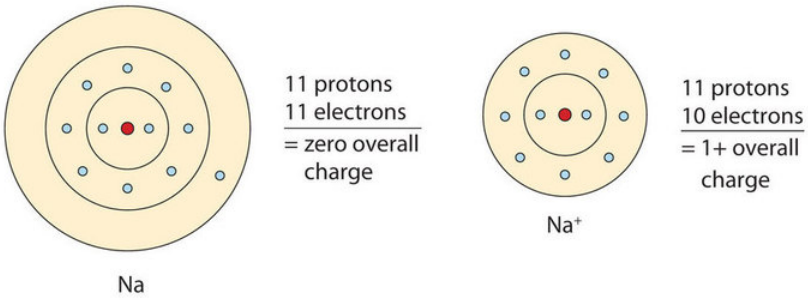


Figure 3.2.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

Now, let's consider chlorine atom, Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$

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.)

$$\begin{array}{lcl} \mathrm{Cl} + \mathrm{e}^- & \rightarrow & \mathrm{Cl}^- \\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5 & & 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 (\text{octet}) \end{array}$$

Figure 3.2.2 is a graphical depiction of this process.

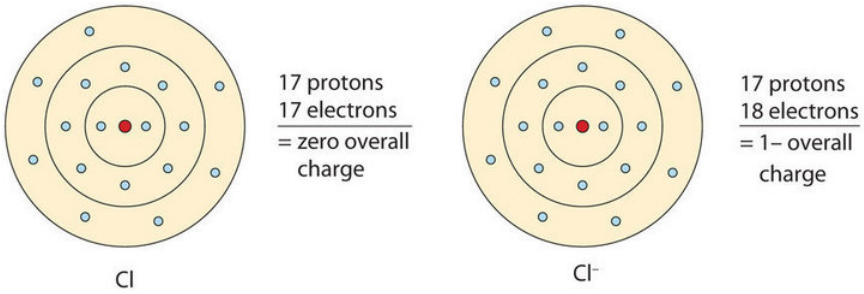


Figure 3.2.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

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 3.2.1

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 $1s^2 2s^2 2p^6 3s^2 3p^1$. The second shell has octet ($2s^2 2p^6$) while the valence shell has 3 electrons ($3s^2 3p^1$). Mg can achieve octet by losing the 3 valence electrons. The resulting cation is Al^{3+} with electron configuration, $1s^2 2s^2 2p^6$.

3.2.1 Exercise

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 $1s^2 2s^2 2p^4$. The second shell has six electrons ($2s^2 2p^4$) and needs two electrons to achieve octet. Oxygen will gain 2 electrons. The resulting anion is O^{2-} with electron configuration, $1s^2 2s^2 2p^6$.

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 3.2.3 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}.

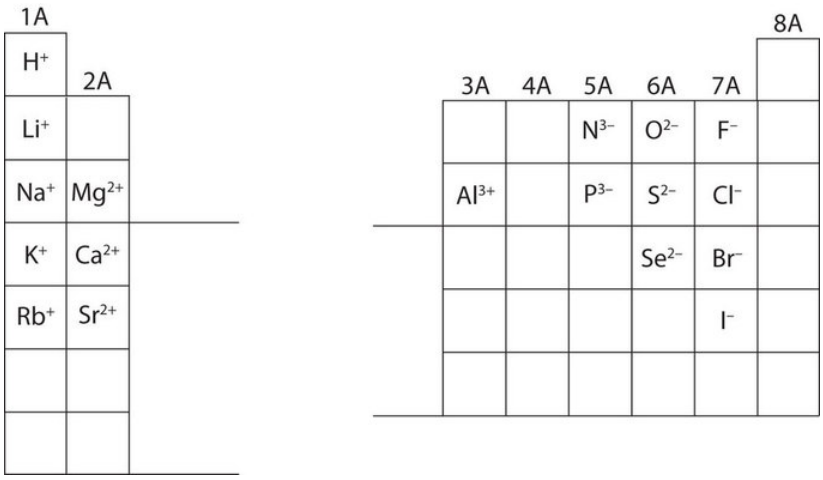


Figure 3.2.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

Example 3.2.2

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.

3.2.2 Exercise

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

a. S^{3-}
b. N^{3-}

Answer

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

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:

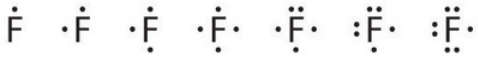
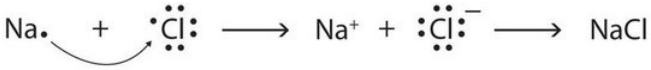


Figure 3.2.4 shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the **main group** elements, the **number of valence electrons** is the **same as the group number** listed at the top of the periodic table.



Figure 3.2.4: Lewis Electron Dot Diagrams of the Elements Lithium through Neon

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



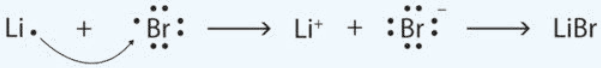
In representing the final formula, the dots are omitted.

Example 3.2.3

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

Solution

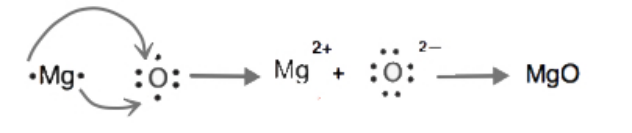
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it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



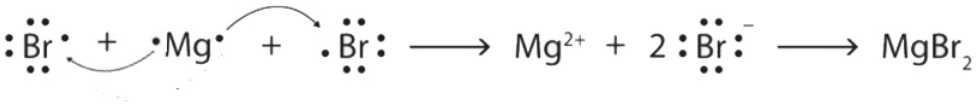
Exercise 3.2.3

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 3.2.5 shows the characteristic charges for some of these ions. As we saw in Figure 3.2.1, 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).

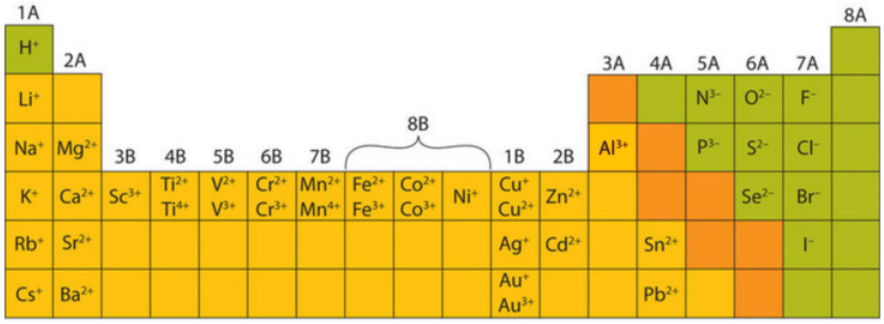


Figure 3.2.5: Charges of the Monatomic Ions. Note that some atoms commonly form ions of variable charges.

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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3.3: Formulas of Ionic Compounds

Learning Objectives

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

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

Ionic Compounds Formed From Monoatomic Ions

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

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

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

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

$$\mathbf{Na}\cdot \rightsquigarrow \cdot\ddot{\underset{\cdot\cdot}{\mathbf{Cl}}}\mathbf{:}$$

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

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

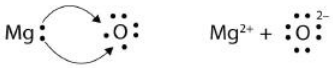
$$[Ne] \qquad [Ne]\,3s^2 3p^6$$

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

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

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

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



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

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

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

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

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

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



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

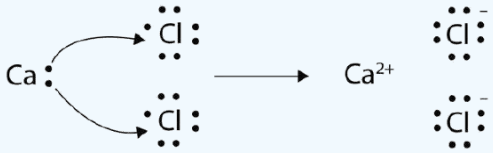
These three ions attract each other to form an overall neutrally charged ionic compound, which we write as Na_2O. The need for the number of electrons lost to be equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is also required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

Example 3.3.1

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

Solution

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



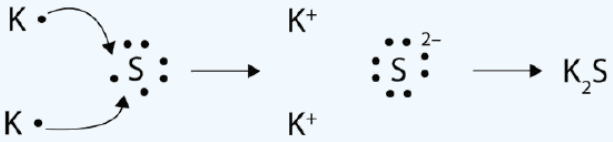
Calcium donates two electrons, one each going to a chlorine. This empties calcium's orbital and fills both of the chlorines'. This creates Ca2+ and two Cl-.

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

Exercise 3.3.1

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

Answer



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

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

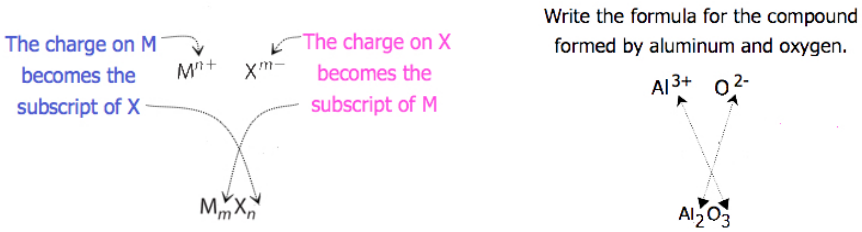


Figure 3.3.1: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

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

Example 3.3.2: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 3.3.2) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Figure 3.3.2: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution

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

Exercise 3.3.2

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

Answer

Na_2S

Ionic Compounds Formed From Polyatomic Ions

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

Example 3.3.3: Predicting the Formula of a Compound with a Polyatomic Anion

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

Solution

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

Exercise 3.3.3

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

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

Answer a:

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

Answer b:

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

Formula Unit

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 3.3.3). As you can see, there are no individual NaCl "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers or *simplest formula*, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use NaCl (one Na symbol and one Cl symbol) to represent the compound. Thus, NaCl is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that NaCl crystals are composed of individual NaCl units, Figure 3.3.3 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

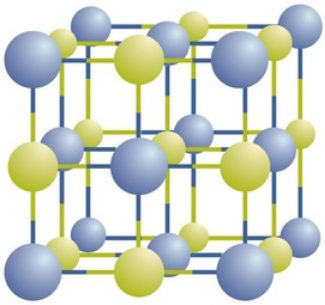


Figure 3.3.3: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

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3.4: Naming Ionic Compounds

Learning Objectives

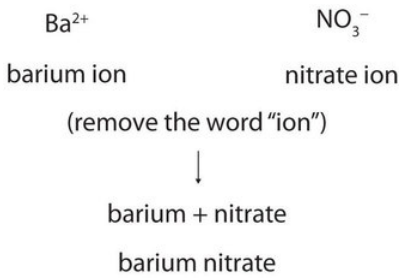
- Write the names for ionic compounds by recognizing and naming the ions in the formula unit.

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

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

Type I Ionic Compounds

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



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

Type II Ionic Compounds

Some metals can form cations with variable charges. When naming a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $\mathrm{FeCl_2}$ and $\mathrm{FeCl_3}$. In the first compound, the iron ion has a 2+ charge because there are two $\mathrm{Cl^-}$ ions in the formula (1− charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three $\mathrm{Cl^-}$ ions in the formula. These are two different compounds that need two different names. By the *stock system*, the names are iron(II) chloride and iron(III) chloride. If we were to use the stems and suffixes of the *common system*, the names would be ferrous chloride and ferric chloride, respectively.

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 3.4.1. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 3.4.1: Everyday Ionic Compounds

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

As you practice naming compounds, use Figure 3.4.1 as a guide.

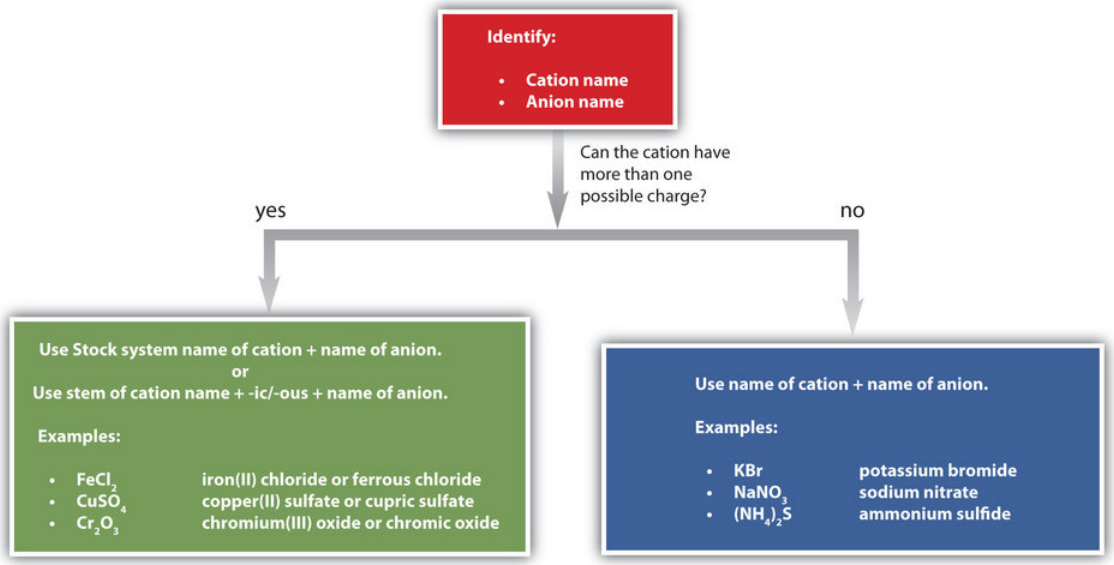


Figure 3.4.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

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

Example 3.4.3

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

a. $Ca_3(PO_4)_2$
b. $(NH_4)_2Cr_2O_7$
c. KCl
d. CuCl
e. SnF_2

Answer a

calcium phosphate

Answer b

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

Answer c

potassium chloride

Answer d

copper(I) chloride or cuprous chloride

Answer e

tin(II) fluoride or stannous fluoride

Exercise 3.4.3

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

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

Answer a

zinc bromide

Answer b

iron (III) nitrate or ferric nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride or cupric fluoride

Answer e

silver fluoride

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3.5: 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 3.5.1

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 3.5.1

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 $CuSO_4 \cdot 5\,H_2O$. 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 ($CaSO_4 \cdot ½H_2O$), known as plaster of Paris, is used to make casts for broken bones. Epsom salt ($MgSO_4 \cdot 7\,H_2O$) 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 3.5.1: Names and Formulas of Some Widely Used Hydrates

Formula	Name	Uses
$AlCl_3$•$6H_2O$	aluminum chloride hexahydrate	antiperspirant
$CaSO_4$•$½H_2O$	calcium sulfate hemihydrate (plaster of Paris)	casts (for broken bones and castings)
$CaSO_4$•$2H_2O$	calcium sulfate dihydrate (gypsum)	drywall component
$CoCl_2$•$6H_2O$	cobalt(II) chloride hexahydrate	drying agent, humidity indicator
$CuSO_4$•$5H_2O$	copper(II) sulfate pentahydrate	fungicide, algicide, herbicide
$MgSO_4$•$7H_2O$	magnesium sulfate heptahydrate (Epsom salts)	laxative, bathing salt
Na_2CO_3•$10H_2O$	sodium carbonate decahydrate (washing soda)	laundry additive/cleaner

KEY TAKEAWAY

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

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3.6: Some Properties of Ionic Compounds

Learning Objectives

- Describe the basic physical properties of ionic compounds.

The figure below shows just a few examples of the color and brilliance of naturally occurring ionic crystals. The regular and orderly arrangement of ions in the crystal lattice is responsible for the various shapes of these crystals, while transition metal ions give rise to the colors.

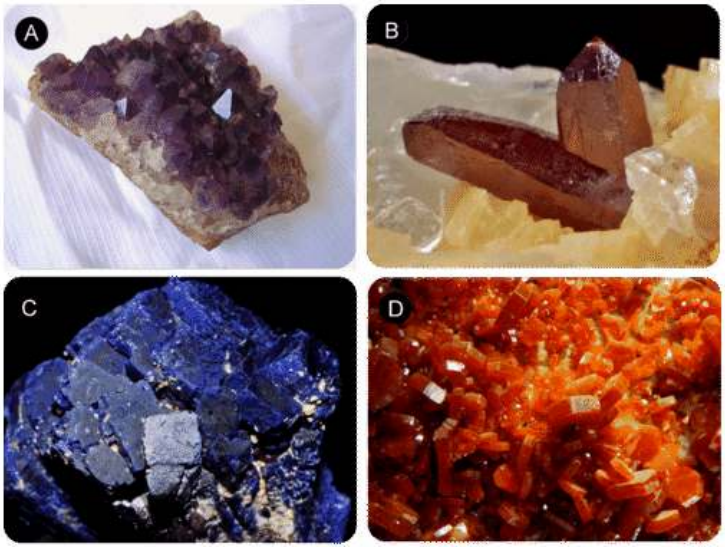


Figure 3.6.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz, SiO_2, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral, $Cu_3(CO_3)_2(OH)_2$. (D) Vanadinite - the primary ore of vanadium, $Pb_3(VO_4)_3Cl$.*

Melting Points

Because of the many simultaneous attractions between cations and anions that occur, ionic crystal lattices are very strong. The process of melting an ionic compound requires the addition of large amounts of energy in order to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about 800 ^oC. As a comparison, the molecular compound water melts at 0 °C.

Shattering

Ionic compounds are generally hard, but **brittle.** Why? It takes a large amount of mechanical force, such as striking a crystal with a hammer, to force one layer of ions to shift relative to its neighbor. However, when that happens, it brings ions of the same charge next to each other (see below). The repulsive forces between like-charged ions cause the crystal to shatter. When an ionic crystal breaks, it tends to do so along smooth planes because of the regular arrangement of the ions.

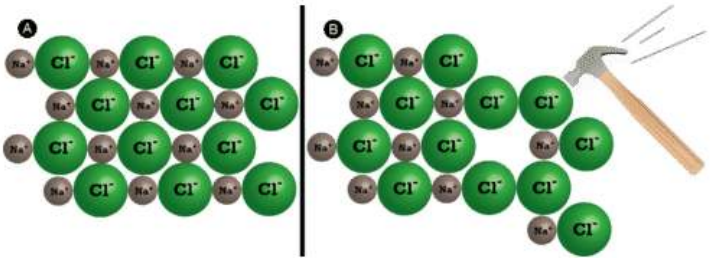


Figure 3.6.2: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

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.

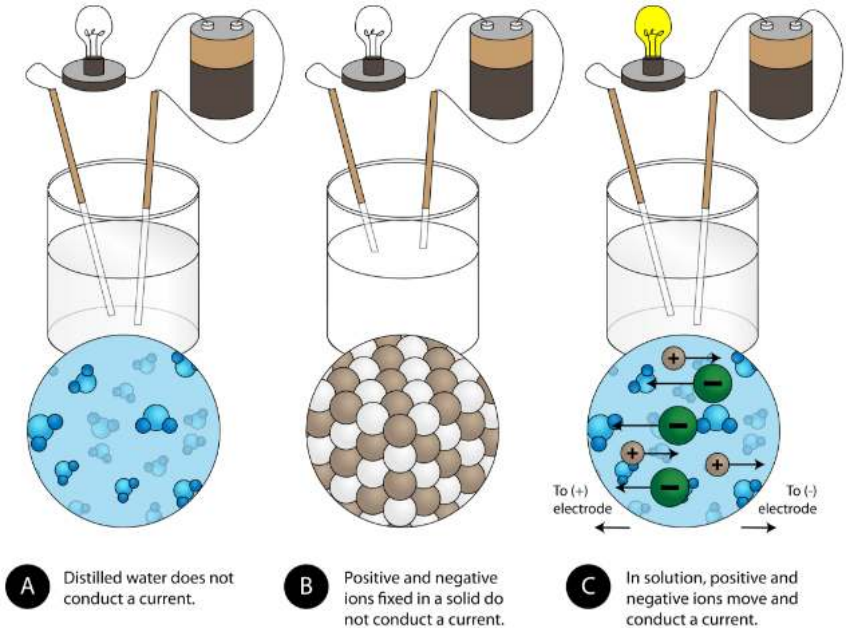


Figure 3.6.3: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

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.

Example 3.6.1

Write the dissociation equation of solid NaCl in water.

Solution

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

Exercise 3.6.1

Write the dissociation equation of solid NH_4NO_3 in water.

Answer

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

Key Takeaways

- Ionic compounds have high melting points.
- Ionic compounds are hard and brittle.
- Ionic compounds dissociate into ions when dissolved in water.
- Solutions of ionic compounds and melted ionic compounds conduct electricity, but solid materials do not.
- An ionic compound can be identified by its chemical formula: metal + nonmetal or polyatomic ions.

Contributors and Attributions

- CK-12 Foundation by Sharon Bewick, Richard Parsons, Therese Forsythe, Shonna Robinson, and Jean Dupon.

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3.E: Ionic Bonding and Simple Ionic Compounds (Exercises)

Chapter Exercises

3.1: Two Types of Bonding

1. What is the octet rule?

2. How are ionic bonds formed?

3. Why is an ionic compound unlikely to consist of two positively charged ions?

4. Why is an ionic compound unlikely to consist of two negatively charged ions?

5. A calcium atom has two valence electrons. Do you think it will lose two electrons or gain six electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

6. An aluminum atom has three valence electrons. Do you think it will lose three electrons or gain five electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

7. A selenium atom has six valence electrons. Do you think it will lose six electrons or gain two electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

8. An iodine atom has seven valence electrons. Do you think it will lose seven electrons or gain one electron to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

3.2: Ions

1. What are the two types of ions?
2. Use Lewis diagrams to illustrate the formation of an ionic compound from a potassium atom and an iodine atom.

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

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

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

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

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

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

6. Write the electron configuration for each ion.

a. Li^+
b. Mg^{2+}

c. F^-
d. S^{2-}

7. Write the electron configuration for each ion.

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

8. Draw Lewis diagrams for the ions listed in Exercise 6. Also include Lewis diagrams for the respective neutral atoms as a comparison.

9. Draw Lewis diagrams for the ions listed in Exercise 7. Also include Lewis diagrams for the respective neutral atoms as a comparison.

10. Using Lewis diagrams, show the electron transfer for the formation of LiF.

11. Using Lewis diagrams, show the electron transfer for the formation of MgO.

12. Using Lewis diagrams, show the electron transfer for the formation of Li_2O.

13. Using Lewis diagrams, show the electron transfer for the formation of CaF_2.

14. What characteristic charge do atoms in the first column of the periodic table have when they become ions?

15. What characteristic charge do atoms in the second column of the periodic table have when they become ions?

16. What characteristic charge do atoms in the third-to-last column of the periodic table have when they become ions?

17. What characteristic charge do atoms in the next-to-last column of the periodic table have when they become ions?

3.5: Formula Mass

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

3.1: Two Types of Bonding

1. The octet rule is the concept that atoms tend to have eight electrons in their valence electron shell.

2. Ionic bonds are formed by the attraction between oppositely charged ions.

3. Positive charges repel each other, so an ionic compound is not likely between two positively charged ions.

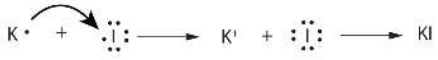
4. Negative charges repel each other also. 5. Ca atom is more likely to lose two electrons. It will become Ca^{2+} ion. 6. An Al atom is more likely to lose three electrons. It will become Al^{3+} ion.

7. Selenium is more likely to gain two electrons. It will become Se^{2-} ion.

8. Iodine is more likely to gain one electron. It will become I^- ion.

3.2: Ions

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

2. 

3. a. 1+

b. 2−
c. 2+
d. 1−

4.

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

5.

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

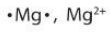
6.

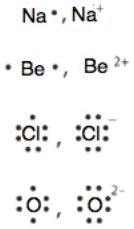
a. $1s^2$
b. $1s^22s^22p^6$
c. $1s^22s^22p^6$
d. $1s^22s^22p^63s^23p^6$

7.

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

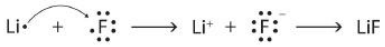
8.

a. 
b. 
c. 
d. 

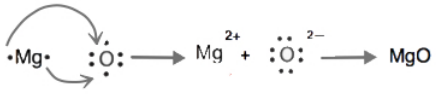


9.

10.



11.



12.



13.

14. 1+

15. 2+

16. 2−

17. 1−

3.5: Formula Mass

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.

https://chem.libretexts.org/@go/page/469229

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

Additional Exercises

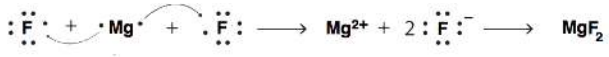
1. What number shell is the valence electron shell of a sodium atom? What number shell is the valence shell of a sodium ion? Explain the difference.
2. What number shell is the valence electron shell of a bromine atom? What number shell is the valence shell of a bromide ion? Explain the difference between these answers and the answers to Exercise 1.
3. What is the electron configuration of each ion?
    1. K^+
    2. Mg^{2+}
    3. F^-
    4. S^{2-}
4. What is the electron configuration of each ion?
    1. Li^+
    2. Ca^{2+}
    3. Cl^-
    4. O^{2-}
5. 1. If a sodium atom were to lose two electrons, what would be the electron configuration of the resulting cation?
    2. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 5a to suggest why sodium atoms do not form a 2+ cation.
6. 1. If a chlorine atom were to gain two electrons, what would be the electron configuration of the resulting anion?
    2. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 6a to suggest why chlorine atoms do not form a 2− anion.
7. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among Mg atoms and F atoms. (Hint: how many atoms of each will you need?)

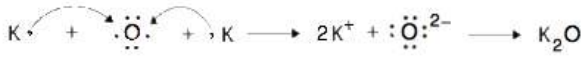
8. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among K atoms and O atoms. (Hint: how many atoms of each will you need?)
9. Mercury forms two possible cations—Hg^{2+} and Hg_2^{2+}, the second of which is actually a two-atom cation with a 2+ charge.
    1. Using common names, give the probable names of these ions.
    2. What are the chemical formulas of the ionic compounds these ions make with the oxide ion, O^{2-}?
10. The uranyl ion (UO_2^{2+}) is a common water-soluble form of uranium. What is the chemical formula of the ionic compound uranyl nitrate? What is the chemical formula of the ionic compound uranyl phosphate?
11. The formal chemical name of the mineral *strengite* is iron(III) phosphate dihydrate. What is the chemical formula of strengite? What is the formula mass of strengite?
12. What is the formula mass of $MgSO_4 \cdot 7H_2O$?
13. What is the formula mass of $CaSO_4 \cdot ½H_2O$?
14. What mass does 20 formula units of NaCl have?
15. What mass does 75 formula units of K_2SO_4 have?
16. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of one formula unit of NaCl?
17. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of 5.00×10^{22} formula units of NaOH?
18. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of 3.96×10^{23} formula units of $(NH_4)_2SO_4$?
19. Both tin and lead acquire 2+ or 4+ charges when they become ions. Use the periodic table to explain why this should not surprise you.
20. Which ion would you expect to be larger in size—In^{3+} or Tl^{3+}? Explain.
21. Which ion would you expect to be smaller in size—I^- or Br^-? Explain.
22. Which ion with a 2+ charge has the following electron configuration? $1s^2 2s^2 2p^6$
23. Which ion with a 3− charge has the following electron configuration? $1s^2 2s^2 2p^6$

Answers

1. For sodium, the valence shell is the third shell; for the sodium ion, the valence shell is the second shell because it has lost all its third shell electrons.
2. The valence shell for both bromine atom and bromide ion is n=4. This is because the valence shell of bromine atom can accommodate one more electron.
3. 1. $1s^2 2s^2 2p^6 3s^2 3p^6$
    2. $1s^2 2s^2 2p^6$
    3. $1s^2 2s^2 2p^6$
    4. $1s^2 2s^2 2p^6 3s^2 3p^6$
4. 1. $1s^2$
    2. $1s^2 2s^2 2p^6 3s^2 3p^6$
    3. $1s^2 2s^2 2p^6 3s^2 3p^6$
    4. $1s^2 2s^2 2p^6$
5. 1. $1s^2 2s^2 2p^5$
    2. It probably requires too much energy to form.
6. 1. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

2. Gaining the second electron would probably require too much energy.

7. 

8. 

9. 1. mercuric and mercurous, respectively

2. HgO and Hg_2O, respectively

10. uranyl nitrate $UO_2(NO_3)_2$ and uranyl phosphate $(UO_2)_3(PO4)_2$

11. $FePO_4 \cdot 2H_2O$; 186.86 u

12. 246.51 u

13. 145.16 u

14. 1,169 u

15. 13,070 u

16. 9.701 x 10^{-23} g

17. 3.32 g

18. 86.9 g

19. Both tin and lead have two *p* electrons and two *s* electrons in their valence shells.

20. Tl^{3+} is larger because it is found lower on the periodic table

21. Br^- because it is higher up on the periodic table

22. Mg^{2+}

23. N^{3-}

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3.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.

The **formula mass** of an ionic compound is the sum of the masses of each individual atom in the formula. Care must be taken when calculating formula masses for formulas containing multiple polyatomic ions because the subscript outside the parentheses refers to all the atoms in the polyatomic ion.

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

4: 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.

4.0: Prelude to Covalent Bonding and Simple Molecular Compounds
4.1: Covalent Bonds
4.2: Covalent Compounds- Formulas and Names
4.3: Drawing Lewis Structures
4.4: The Shapes of Molecules
4.5: Polar Covalent Bonds and Electronegativity
4.6: Polar Molecules
4.7: Organic Chemistry
4.E: Covalent Bonding and Simple Molecular Compounds (Exercises)
4.S: Covalent Bonding and Simple Molecular Compounds (Summary)

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4.0: 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.

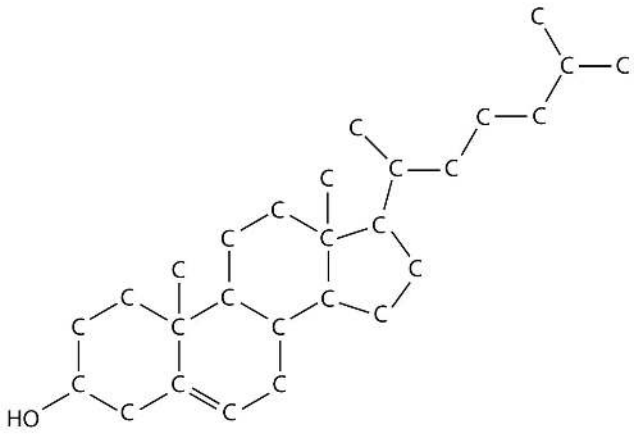


Figure 4.0.1: A Molecular Model of Cholesterol

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4.1: Covalent Bonds

Learning Objectives

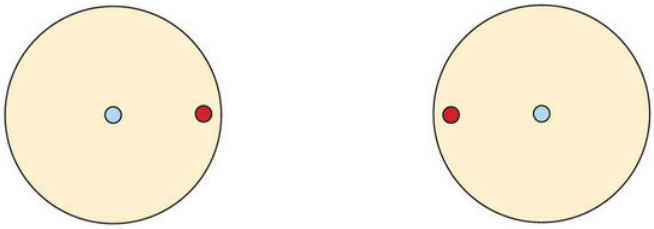
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

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.

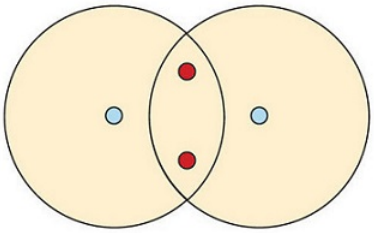
Electron Sharing

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



Two F's with two dots in between them, and two dots on the top, left/right side, and bottoms of each F.

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:



Two F's with a long dash in between them, and two dots on the top, left/right side, and bottoms of each F.

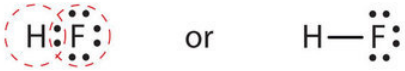
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

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:



An H and F connected by two dots, and the F has 2 dots on the top, right, and bottom. It also shows the same combination but with a long dash in between the H and F rather than two dots.

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 4.1.1

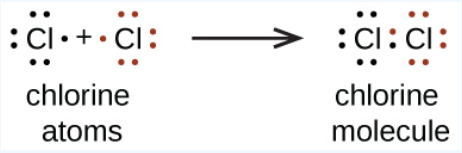
Use Lewis diagrams to indicate the formation of the following:

a. Cl_2
b. HBr

Solution

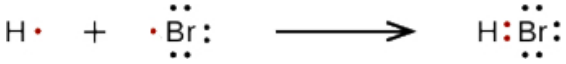
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

The Lewis diagram for a Cl_2 molecule is similar to the one for F_2 (shown above).



Cl with 7 dots surrounding it plus Cl with 7 dots surrounding it means they are chlorine atoms. To turn into a chlorine molecule, have two dots in between each Cl and 6 dots surrounding each Cl on the sides that aren't connected.

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.



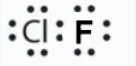
H with one dot plus Br with 7 dots turns into H connected to Br by two dots, with 6 other dots surrounding Br.

Exercise 4.1.1

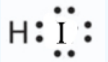
Draw the Lewis diagram for each compound.

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:

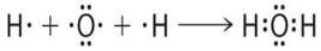


Answer b:



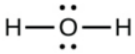
Covalent Bonds in Larger Molecules

The formation of a water molecule from two hydrogen atoms and an oxygen atom can be illustrated using Lewis dot symbols (shown below).



H with one dot + O with 6 dots + H with one dot turns into H connected to O with two dots connected to H with two dots. O also has two dots on top and top dots on bottom.

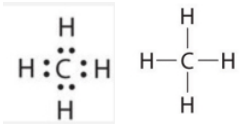
The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



Water

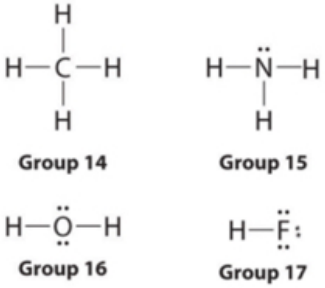
Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis

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.

This table shows atoms and their group numbers, and how many bonds and lone pairs each has.

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 4.1.1 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.

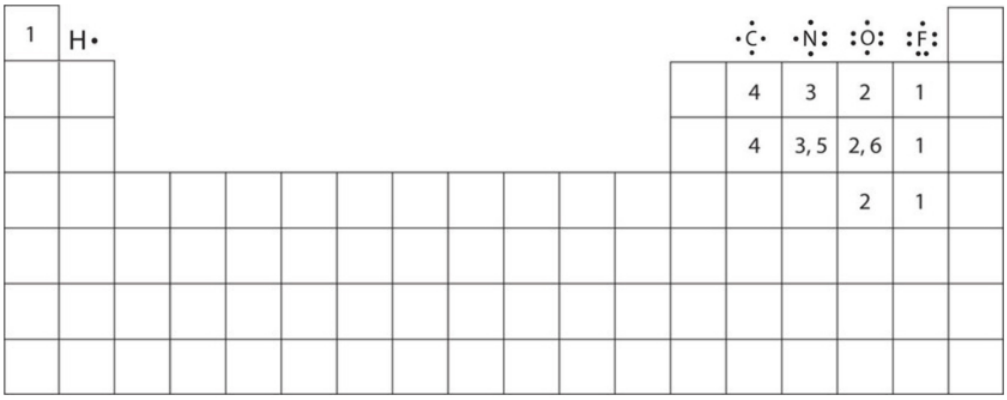
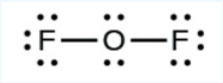


Figure 4.1.1: How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.

Example 4.1.2

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?



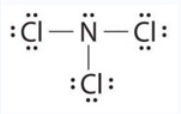
F surrounded by 6 dots, connected to O with a long dash. O surrounded by 4 dots and connects to another F with a long dash. F surrounded by 6 dots.

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.

4.1.2Exercise

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.

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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4.2: Covalent Compounds- Formulas and Names

Learning Objectives

- Understand the different ways to represent molecules.
- Name binary molecular compounds.

Molecular Formulas

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

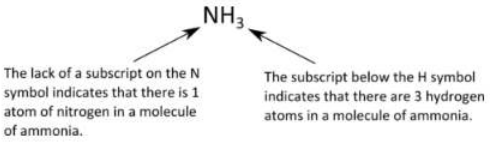


Figure 4.2.2: The molecular formula for ammonia. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

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

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

Figure 4.2.3 shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (Figure 4.2.3*a*) gives only the number of each kind of atom; writing methanol as CH_4O tells nothing about its structure. In contrast, the structural formula (Figure 4.2.3*b*) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure 4.2.3) and the perspective drawing (Figure 4.2.3*d*) show the three-dimensional structure of the molecule. The latter (also called a wedge-and-dash representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure 4.2.3) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. In addition, in a space-filling model, atoms at the "front" of the molecule may obscure atoms at the "back."

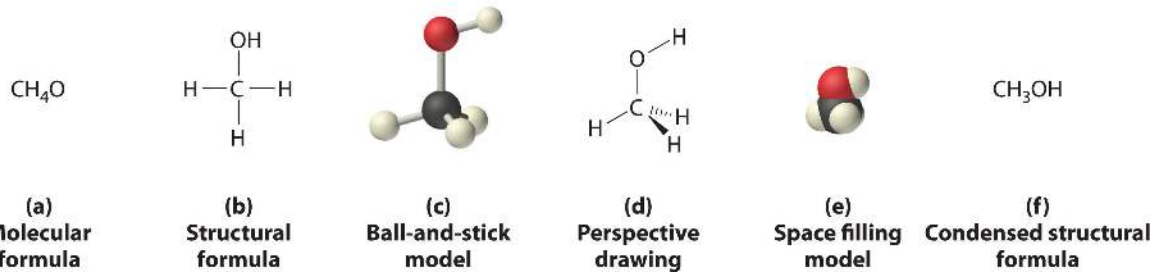


Figure 4.2.3: Different Ways of Representing the Structure of a Molecule. (a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a condensed structural formula (part (f) in Figure 4.2.3), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is CH_3OH, which indicates that the molecule contains a CH_3 unit that looks like a fragment of methane (CH_4). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

Example 4.2.1: Molecular Formulas

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

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

Given: condensed structural formula

Asked for: molecular formula

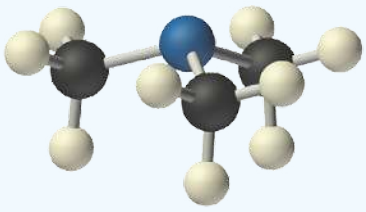
Strategy:

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

Solution:

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

a. **A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula S_2Cl_2.
b. **A** Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and hydrogen atoms, so it is organic. **B** As with all organic compounds, C and H are written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $C_2H_6O_2$.
c. **A** The condensed structural formula shows that trimethylamine contains three CH_3 units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. **B** According to the convention for organic compounds, C and H are written first, giving the molecular formula C_3H_9N.



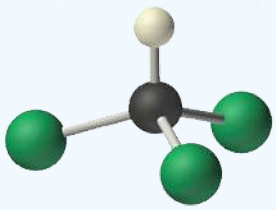
Trimethylamine

https://chem.libretexts.org/@go/page/469234

? Exercise 4.2.1: Molecular Formulas

Write the molecular formula for each molecule.

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



Chloroform

Answer a

$CHCl_3$

Answer b

N_2H_4

Answer c

Name binary molecular compounds.

Naming *binary* (two-element) covalent compounds is very similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. Unlike for ionic compounds, molecular compounds can be formed using the same elements in different ratios. Therefore, it is important to indicate the number of each type of atom, using a system of numerical prefixes, listed in Table 4.2.1. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table 4.2.1: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

*This prefix is not used for the first element's name.

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

Example 4.2.1

Write the molecular formula for each compound.

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

Solution

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

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

Exercise 4.2.1

Write the molecular formula for each compound.

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

Answer a:

a. NO_2

Answer b:

O_2F_2

Answer c:

SF_6

Answer d:

SeO

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

Example 4.2.2

Write the name for each compound.

a. BrF_5
b. S_2F_2
c. CO

Solution

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

Exercise 4.2.2

Write the name for each compound.

a. CF_4
b. $SeCl_2$
c. SO_3

Answer a:

carbon tetrafluoride

Answer b:

selenium dichloride

Answer c:

sulfur trioxide

For some simple covalent compounds, we use common names rather than systematic names. We have already encountered these compounds, but we list them here explicitly:

- H_2O: water
- NH_3: ammonia
- CH_4: methane

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

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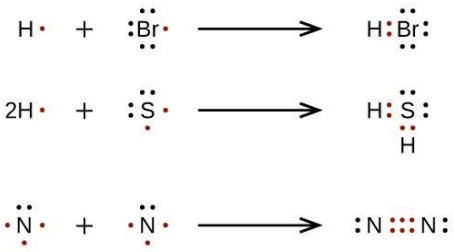
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4.3: Drawing Lewis Structures

Learning Objectives

- Draw Lewis structures for molecules.

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



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

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

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

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

The H_2O Molecule

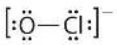
1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each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



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

The OCl^- Ion

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



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

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

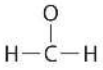
The CH_2O Molecule

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



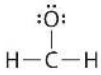
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

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



Six electrons are used, and 6 are left over.

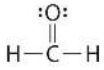
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



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

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

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



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

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

Example 4.3.1

Write the Lewis electron structure for each species.

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

Given: chemical species

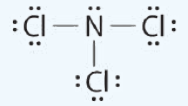
Asked for: Lewis electron structures

Strategy:

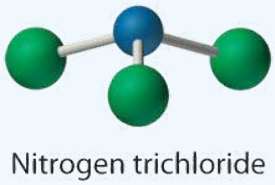
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

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



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



Nitrogen trichloride

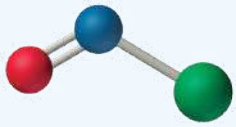
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons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

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

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

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

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



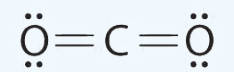
Nitrosyl chloride

? Exercise 4.3.1

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

Answer

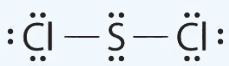
1.



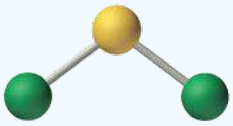


Carbon dioxide

2.



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



Sulfur dichloride

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4.4: The Shapes of Molecules

Learning Objectives

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

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

The VSEPR Model

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

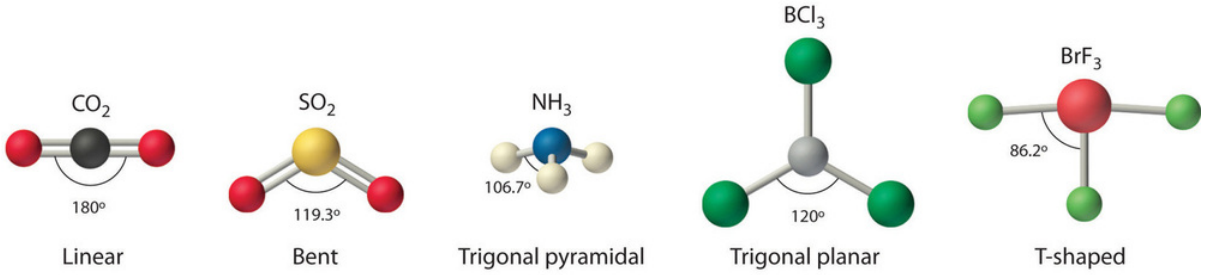


Figure 4.4.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form **electron groups** (regions of electron density), which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 4.4.1.

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

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

Predicting Electron Group Geometry and Molecular Structure

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

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

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

Table 4.4.1 summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table 4.4.1: Summary of Electron Group Geometries and Molecular Structures

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

Two Electron Groups

Any molecule with only two atoms is **linear**. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible, which is 180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular structure is linear. Examples include BeH_2 and CO_2:



Figure 4.4.2: Beryllium hydride and carbon dioxide bonding.

Three Electron Groups

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle, 120° apart and in a plane. The shape of such molecules is **trigonal planar**. An example is BF_3:

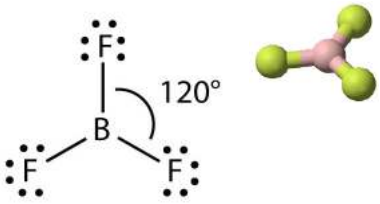


Figure 4.4.3: Boron trifluoride bonding. (CK12 Licence)

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:

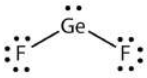


Figure 4.4.4: Germanium difluoride bonding.

From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This molecular structure is called **bent 120°** or angular.

Four Electron Groups

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



Figure 4.4.5: Tetrahedral structure of methane. (CK12 Licence)

This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

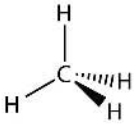


Figure 4.4.6: Methane bonding. (CK12 Licence)

NH_3 is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.

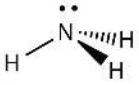


Figure 4.4.7: Ammonia bonding. (CK12 Licence)

Although the electron groups are oriented in the shape of a *tetrahedron*, from a molecular geometry perspective, the shape of NH_3 is **trigonal pyramidal**.

H_2O is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.

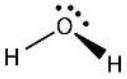


Figure 4.4.8: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is **bent 109°** or angular. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom, is linear because there are only two atoms in the molecule.

Shapes of Molecules with Double or Triple Bonds

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure 4.4.9.



Figure 4.4.9: Lewis Electron Dot Diagram of Formaldehyde.

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a *trigonal planar shape*.

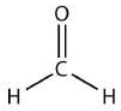


Figure 4.4.10: Formaldehyde bonding.

(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

Example 4.4.1

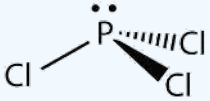
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

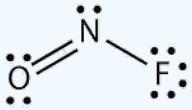
The first step is to draw the Lewis structure of the molecule.

For PCl_3, the electron dot diagram is as follows:



The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

The electron dot diagram for NOF is as follows:



The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

Exercise 4.4.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

Exercise 4.4.2

Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule. (Hint: hydrogen is a terminal atom.)

Answer

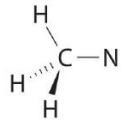
Trigonal planar about both central C atoms.

Molecules With Multiple Central Atoms

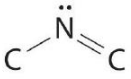
The VSEPR model can be used to predict the structure of somewhat more complex molecules with more than one central atom by using VSEPR as described above for each central atom individually. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a

volatile and highly toxic molecule that is used to produce the pesticide Sevin.

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



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



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

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

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

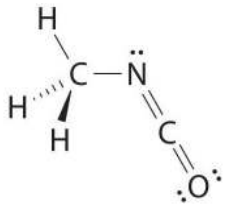


Figure 4.4.11). The Lewis Structure of Methyl Isocyanate

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

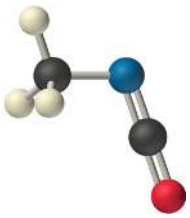


Figure 4.4.12: The Experimentally Determined Structure of Methyl Isocyanate

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

Example 4.4.3

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

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 4.4.3 to determine the molecular geometry around each carbon atom and then deduce the structure of

the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

? Exercise 4.4.3

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

Answer

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

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4.5: Polar Covalent Bonds and Electronegativity

Learning Objectives

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

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

Bond Polarity

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

- A **nonpolar covalent bond** (Figure 4.5.1*a*)is one in which the electrons are shared *equally* between two atoms.
- A **polar covalent bond** (Figure 4.5.1*b*) is one in which one atom has a greater attraction for the electrons than the other atom.
- If the relative attraction of an atom for electrons is great enough, then the bond is an **ionic bond (**Figure 4.5.1*c*).

Electron density in a polar bond is distributed unevenly and is greater around the atom that attracts the electrons more than the other. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Note that the shaded area around Cl in Figure 4.5.1*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).

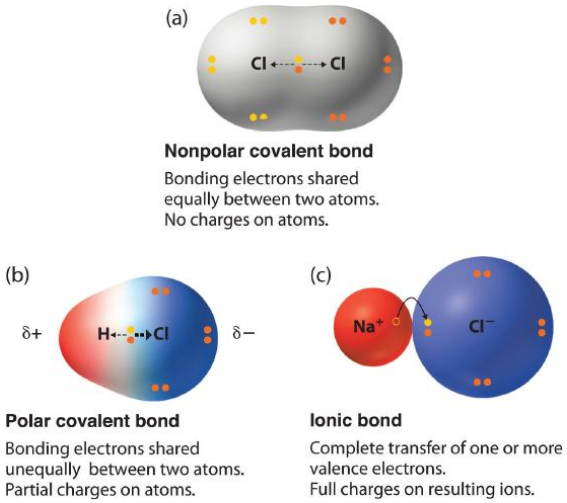


Figure 4.5.1: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in

polarity, with electrons being transferred rather than shared. To judge the relative polarity of a covalent bond, chemists use electronegativity, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

Electronegativity

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

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

Electronegativity is a function of:

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

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

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

The Pauling Electronegativity Scale

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

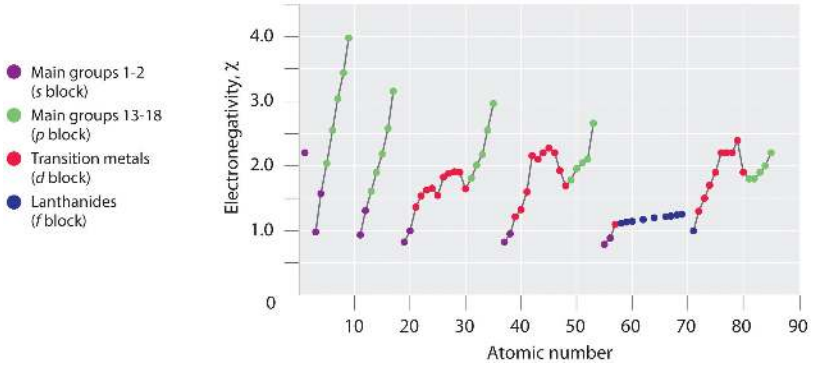


Figure 4.5.2: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table
The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations (trends) in Pauling's electronegativity values are illustrated in Figures 4.5.2 and 4.5.3. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine is the most electronegative element and cesium is the least electronegative nonradioactive element. Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl, and N, S, and Br).

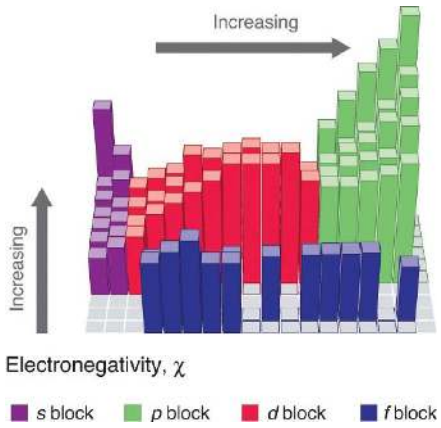


Figure 4.5.3: Pauling Electronegativity Values of the *s*-, *p*-, *d*-, and *f*-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960).

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

The polarity of a covalent bond can be judged by determining the difference in the electronegativities of the two atoms making the bond. The greater the difference in electronegativities, the greater the imbalance of electron sharing in the bond. Although there are no hard and fast rules, the general rule, (see Figure 4.5.5), is if the difference in electronegativities is less than about 0.4, the bond is considered nonpolar; if the difference is greater than 0.4, the bond is considered polar. If the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond.

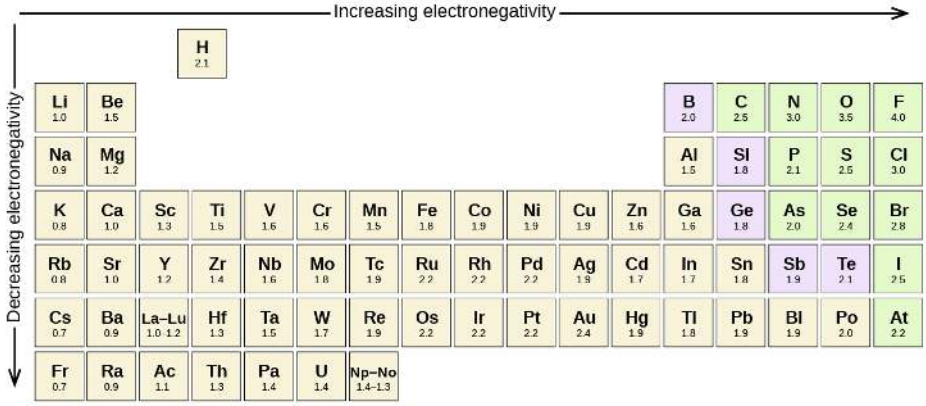
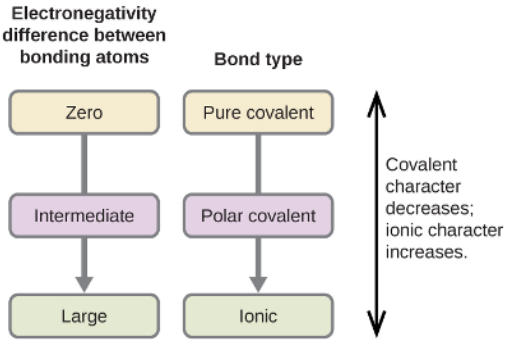


Figure 4.5.4 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).



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

Figure 4.5.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

Example 4.5.1

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

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

Solution

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

Exercise 4.5.1

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:

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

Answer b:

The EN difference is greater than 1.8, hence ionic.

Answer c:

Identical atoms have zero EN difference, hence nonpolar.

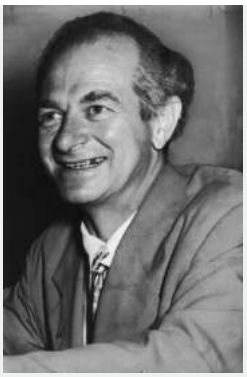
Answer d:

The EN difference is greater than 1.8, hence ionic.

Looking Closer: Linus Pauling

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

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



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

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

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4.6: Polar Molecules

Learning Objectives

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

If there is only one bond in the molecule, the bond polarity determines the *molecular polarity*. Any diatomic molecule in which the two atoms are the same element must be a nonpolar molecule. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule where one end of the molecule is slightly positive, while the other end is slightly negative. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. Hence, a molecule with two poles has a **dipole moment**.

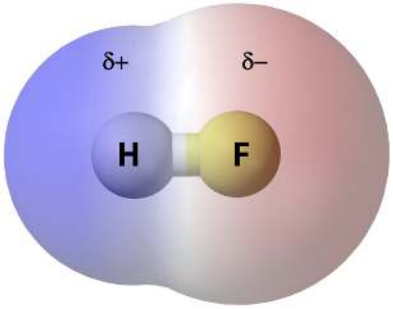


Figure 4.6.1: A molecular dipole results from the unequal distribution of electron density throughout a molecule. The H, with less electron density is partially positive and the F, with more electron density is partially negative. (Figure modified from: Wikipedia [en.Wikipedia.org])

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water.

Carbon dioxide (CO_2) is a linear molecule with carbon in the center and two oxygens at the terminal ends. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and pointing in opposite directions, they *cancel out* and the overall molecular polarity of CO_2 is zero (no net dipole), therefore CO_2 is a *nonpolar molecule*.

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

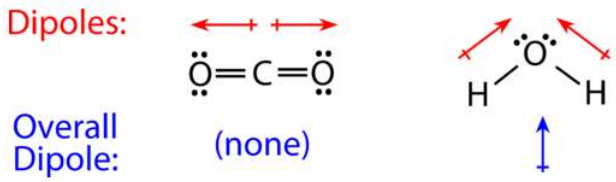


Figure 4.6.2: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. In contrast, water is polar because the OH bond dipole moments do not cancel out. There is a net separation of charge or overall dipole moment.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CH_4 is nonpolar. However, if one of the peripheral H atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule (BF_3) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule (NH_3) is polar.

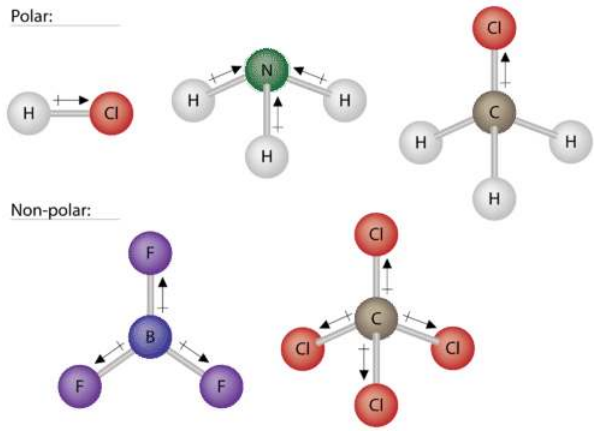


Figure 4.6.3: Some examples of polar and nonpolar molecules based on molecular geometry.

To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment do not cancel.

Steps to Identify Polar Molecules

1. Draw the Lewis structure.
2. Figure out the geometry (using VSEPR theory).
3. Visualize or draw the geometry.
4. Find the net dipole moment (you don't have to actually do calculations if you can visualize it).
5. If the net dipole moment is zero, it is non-polar. Otherwise, it is polar.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 4.6.4). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

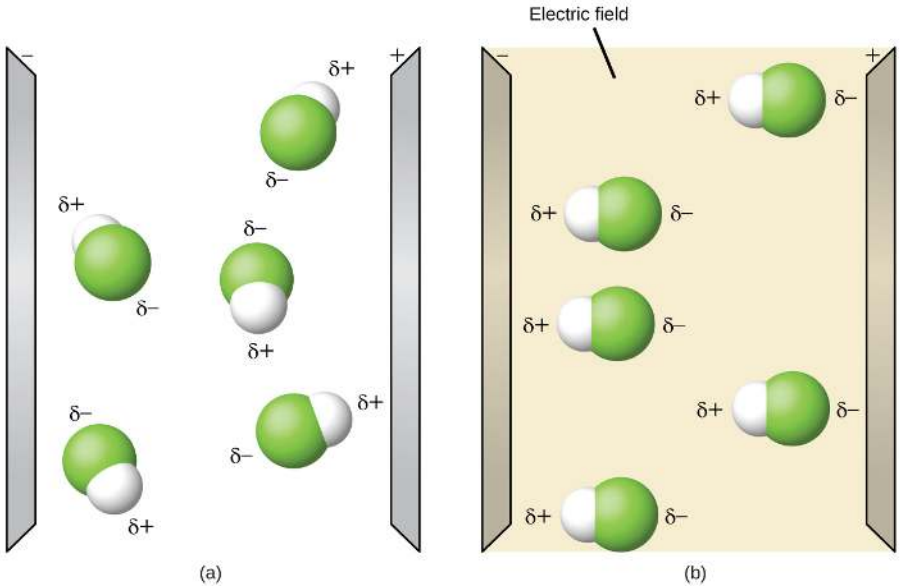


Figure 4.6.4: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

While molecules can be described as "polar covalent" or "ionic", it must be noted that this is often a relative term, with one molecule simply being *more polar* or *less polar* than another. However, the following properties are typical of such molecules. Polar molecules tend to:

- have higher melting points than nonpolar molecules
- have higher boiling points than nonpolar molecules
- be more soluble in water (dissolve better) than nonpolar molecules
- have lower vapor pressures than nonpolar molecules

Example 4.6.1: Polarity Simulations

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

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

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

Solution

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

Exercise 4.6.1

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

Answer

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

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4.7: 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 4.7.1 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.

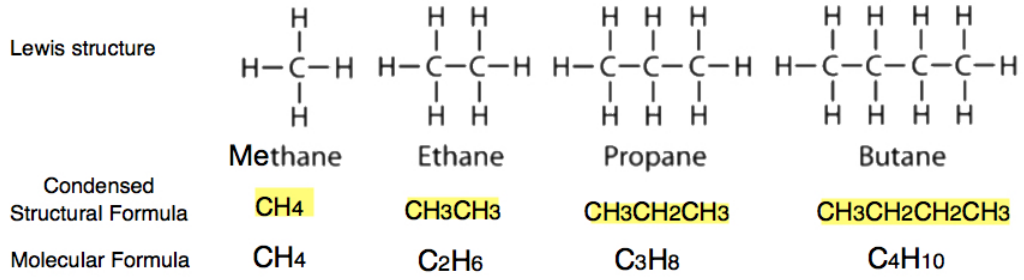


Figure 4.7.1: Formulas and Molecular Models of the Four Simplest Alkanes. The four smallest alkanes are methane, ethane, propane and butane.

Alkenes

Some hydrocarbons have one or more carbon–carbon double bonds (denoted C=C). These hydrocarbons are called alkenes. Figure 4.7.2 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.

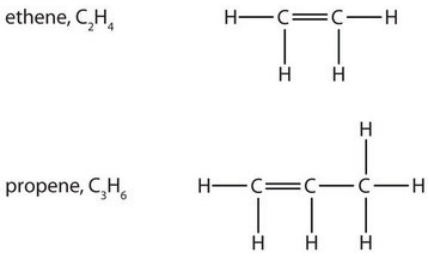
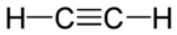


Figure 4.7.2: Formulas and Molecular Models of the Two Simplest Alkenes. Ethene is commonly called ethylene, while propene is commonly called propylene.

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 4.7.4 shows their formulas along with a molecular model of each.

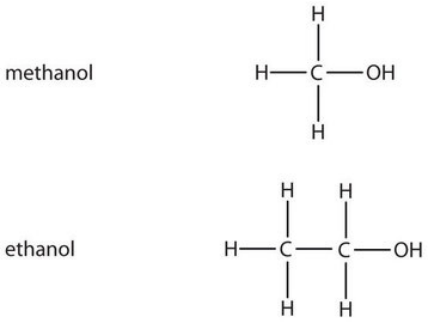


Figure 4.7.4: The Two Simplest Organic Alcohol Compounds. Alcohols have an OH functional group in the molecule.

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 4.7.5 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.

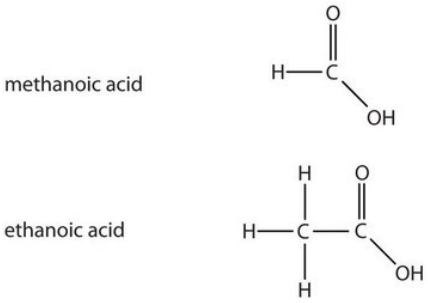


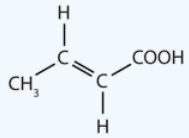
Figure 4.7.5: The Two Smallest Organic Acids. The two smallest carboxylic acids are formic acid (found in the stingers of ants) and acetic acid (found in vinegar).

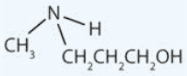
The condensed structures of methanoic acid and ethanoic acid are **HCOOH** and **CH_3COOH**, respectively.

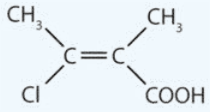
Many organic compounds are considerably more complex than the examples described here. Many compounds, such as cholesterol discussed in the chapter-opening essay, contain more than one functional group. The formal names can also be quite complex.

Example 4.7.1

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.

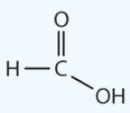
Answer d

This molecule has an alcohol functional group.

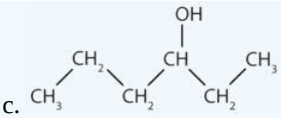
Exercise 4.7.1

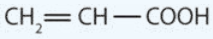
Identify the functional group(s) in each molecule as a double bond, a triple bond, an alcohol, or a carboxyl.

a. $CH_3C \equiv CCH_3$

b. 

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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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4.E: Covalent Bonding and Simple Molecular Compounds (Exercises)

4.1: Covalent Bonds

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?

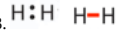
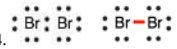
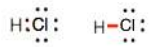
Answers

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

Exercises

1. Define *covalent bond*.
2. What is electron sharing?
3. Draw the Lewis diagram for the covalent bond in the H_2 molecule.
4. Draw the Lewis diagram for the covalent bond in the Br_2 molecule.
5. Draw the Lewis diagram for the covalent bond in the HCl molecule.
6. What is the difference between a molecule and a formula unit?
7. Why do hydrogen atoms not follow the octet rule when they form covalent bonds?
8. Draw the Lewis diagram for the covalent bonding in H_2S. How many bonding electrons and nonbonding electrons are in the molecule?
9. Draw the Lewis diagram for the covalent bonding in CF_4. How many bonding electrons and nonbonding electrons are in the molecule?
10. Draw the Lewis diagram for the covalent bonding in PCl_3. How many bonding electrons and nonbonding electrons are in the molecule?
11. How many covalent bonds does a hydrogen atom typically form? Why?
12. How many covalent bonds does an oxygen atom typically form? Why?
13. Tellurium atoms make covalent bonds. How many covalent bonds would a tellurium atom make? Predict the formula of a compound between tellurium and hydrogen.
14. Tin atoms make covalent bonds. How many covalent bonds would a tin atom make? Predict the formula of a compound between tin and hydrogen.
15. Astatine is a synthetic element, made one atom at a time in huge “atom-smasher” machines. It is in the halogen group on the periodic table. How many covalent bonds would an atom of this element form?
16. There have been reports that atoms of element 116 (Lv) were made by smashing smaller atoms together. Using the periodic table, determine what column element 116 would be in and suggest how many covalent bonds an atom of this element would form.

Answers

1. A covalent bond is formed when two atoms share electrons.
2. Electron sharing joins two atoms in a covalent bond. This is a more stable arrangement than 2 individual atoms.
3. 
4. 
5. 

6. A molecule is a discrete combination of atoms; a formula unit is the lowest ratio of ions in a crystal. 7. Hydrogen atoms follow the duet rule (not the octet rule). This is because it has only one shell and this shell can only hold 2 electrons.

8. 

bonding electrons: 4; nonbonding electrons: 4

9. 

bonding electrons: 8; nonbonding electrons: 24

10. 

bonding electrons: 6; nonbonding electrons: 20

11. Hydrogen atoms form only one covalent bond because they have only one valence electron to pair.
12. Oxygen atoms form 2 covalent bonds because oxygen atoms have 6 valence electrons (2 lone pairs plus 2 unpaired electrons that are shared to achieve octet).
13. two; H_2Te
14. four: SnH_4

15. one
16. two

4.2: Covalent Compounds - Formulas and Names

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.

Exercises

1. Identify whether each compound has covalent bonds.
   a. NaI
   b. Na_2CO_3
   c. N_2O
   d. SiO_2
2. Identify whether each compound has covalent bonds.
   a. C_2H_6
   b. C_6H_5Cl
   c. $KC_2H_3O_2$
   d. $Ca(OH)_2$
3. Identify whether each compound has ionic bonds, covalent bonds, or both.
   a. Na_3PO_4
   b. K_2O
   c. $COCl_2$
   d. $CoCl_2$
4. Identify whether each compound has ionic bonds, covalent bonds, or both.
   a. $FeCl_3$
   b. $Fe(NO_3)_3$
   c. $(NH_2)_2CO$
   d. SO_3
5. Which is the correct molecular formula—H_4Si or SiH_4? Explain.
6. Which is the correct molecular formula—SF_6 or F_6S? Explain.
7. Write the name for each covalent compound.
   a. SiF_4
   b. NO_2
   c. CS_2
   d. P_2O_5
8. Write the name for each covalent compound.
   a. CO
   b. S_2O_3
   c. BF_3
   d. GeS_2
9. Write the formula for each covalent compound.
   a. iodine trichloride
   b. disulfur dibromide
   c. arsenic trioxide
   d. xenon hexafluoride
10. Write the formula for each covalent compound.
    a. boron trichloride
    b. carbon dioxide
    c. tetraphosphorus decoxide
    d. germanium dichloride
11. Write two covalent compounds that have common rather than systematic names.
12. What is the name of the simplest organic compound? What would its name be if it followed the nomenclature for binary covalent compounds?

Answers

1. a. no
   b. yes
   c. yes
   d. yes
2.

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a. yes
b. yes
c. yes
d. yes

3. a. both
   b. ionic
   c. covalent
   d. ionic

4.

   a. ionic
   b. both
   c. covalent
   d. covalent

5. SiH_4; except for water, hydrogen is almost never listed first in a covalent compound.

6. SF_6; the less electronegative atom (S) is written first

7. a. silicon tetrafluoride
   b. nitrogen dioxide
   c. carbon disulfide
   d. diphosphorus pentoxide

8.

   a. carbon monoxide
   b. disulfur trioxide
   c. boron trifluoride
   d. germanium disulfide

9. a. ICl_3
   b. S_2Br_2
   c. AsO_3
   d. XeF_6

10.

    a. BCl_3
    b. CO_2
    c. P_4O_{10}
    d. $GeCl_2$

11. H_2O and NH_3 (water and ammonia) (answers will vary)
12. CH_4; carbon tetrahydride

4.3: Drawing Lewis Structures

Exercises

1. What is one clue that a molecule has a multiple bond?

2. Draw the Lewis diagram for each of the following.

   a. H_2O

   b. NH_3

   c. C_2H_6

   d. CCl_4

3. Each molecule contains double bonds. Draw the Lewis diagram for each. The first element is the central atom.

   a. CS_2
   b. C_2F_4
   c. $COCl_2$

4. Each molecule contains multiple bonds. Draw the Lewis diagram for each. Assume that the first element is the central atom, unless otherwise noted.

   a. N_2
   b. CO
   c. HCN (The carbon atom is the central atom.)
   d. POCl (The phosphorus atom is the central atom.)

5. Explain why hydrogen atoms do not form double bonds.

6. Why is it incorrect to draw a double bond in the Lewis diagram for MgO?

Answers

1. If single bonds between all atoms do not give all atoms (except hydrogen) an octet, multiple covalent bonds may be present.
2. a.

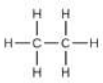


b.



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c.



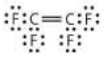
d.



3. a.



b.



c.

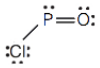


4. a. $\ddot{N} \equiv \ddot{N}$

b. $:C \equiv O:$

c. $H:C \equiv \ddot{N}$

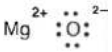
d.



5. Hydrogen can accept only one more electron; multiple bonds require more than one electron pair to be shared.

6. MgO is an ionic compound (Mg transfers two electrons to O). The electrons are not shared hence it's incorrect to draw a double bond.

This is the Lewis dot structure of MgO.



4.4: Characteristics of Covalent Bonds

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

Exercises

1. Which is longer—a C–H bond or a C–O bond? (Refer to Table $4.E.1$.)
2. Which is shorter—an N–H bond or a C–H bond? (Refer to Table $4.E.1$.)
3. A nanometer is 10^{-9} m. Using the data in Table $4.E.1$ and Table $4.E.2$, determine the length of each bond in nanometers.
   a. a C–O bond
   b. a C=O bond
   c. an H–N bond
   d. a C≡N bond
4. An angstrom (Å) is defined as 10^{-10} m. Using Table $4.E.1$ and Table $4.E.2$, determine the length of each bond in angstroms.
   a. a C–C bond
   b. a C=C bond
   c. an N≡N bond
   d. an H–O bond
5. Refer to Exercise 3. Why is the nanometer unit useful as a unit for expressing bond lengths?
6. Refer to Exercise 4. Why is the angstrom unit useful as a unit for expressing bond lengths?
7. Using Figure $4.E.3$, determine which atom in each pair has the higher electronegativity.
   a. H or C
   b. O or Br

c. Na or Rb
d. I or Cl

8. Using Figure 4.E.3, determine which atom in each pair has the lower electronegativity.

a. Mg or O
b. S or F
c. Al or Ga
d. O or I

9. Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

a. a C–O bond
b. an F–F bond
c. an S–N bond
d. an I–Cl bond

10. Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

a. a C–C bond
b. a S–Cl bond
c. an O–H bond
d. an H–H bond

11. Arrange the following bonds from least polar to most polar: H-F, H-N, H-O, H-C

12. Arrange the following bonds from least polar to most polar: C-F, C-N, C-O, C-C

Answers

1. A C–O bond is longer.

2. An H-N bond is shorter than an H-C bond.

3. a. 0.143 nm
b. 0.120 nm
c. 0.100 nm
d. 0.116 nm

4.

a. 1.54 Å
b. 1.34 Å
c. 1.10 Å
d. 0.97 Å

5. Actual bond lengths are very small, so the nanometer unit makes the expression of length easier to understand.

6. Actual bond lengths are very small, so the angstrom unit makes the expression of length easier to understand.

7. a. C
b. O
c. Na
d. Cl

8.

a. Mg
b. S
c. Al
d. I

9.

a. unequally toward the O
b. equally
c. unequally toward the N
d. unequally toward the Cl

10.

a. equally
b. unequally toward the Cl
c. unequally toward the O
d. equally

11. The electronegativity difference increases from 0.4; 0.9; 1.4; 1.9. Hence, the least to most polar: H-C, H-N, H-O, H-F

12. The electronegativity difference increases from 0; 0.5; 1.0; 1.5. Hence, the least to most polar: C-C, C-N, C-O, C-F

4.5: Characteristics of Molecules

Concept Review Exercises

1. How do you determine the molecular mass of a covalent compound?
2. How do you determine the shape of a molecule?
3. How do you determine whether a molecule is polar or nonpolar?

Answers

1. The molecular mass is the sum of the masses of the atoms in the formula.

2. 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.

3. 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.

Exercises

1. What is the molecular mass of each compound?
   a. H_2S
   b. N_2O_4
   c. ICl_3
   d. HCl
2. What is the molecular mass of each compound?
   a. O_2F_2
   b. CCl_4
   c. C_6H_6
   d. SO_3
3. Aspirin ($C_9H_8O_4$) is a covalent compound. What is its molecular mass?
4. Cholesterol ($C_{27}H_{46}O$) is a biologically important compound. What is its molecular mass?
5. What is the shape of each molecule? State whether it is polar or nonpolar.
   a. H_2S
   b. $COCl_2$
   c. SO_2
6. What is the shape of each molecule? State whether it is polar or nonpolar.
   a. NBr_3
   b. SF_2
   c. SiH_4
7. Predict the shape of nitrous oxide (N_2O), which is used as an anesthetic. A nitrogen atom is in the center of this three-atom molecule. Is this polar?
8. Predict the shape of acetylene (C_2H_2), which has the two carbon atoms in the middle of the molecule with a triple bond. What generalization can you make about the shapes of molecules that have more than one central atom?

Answers

1. a. 34.08 amu
   b. 92.02 amu
   c. 233.25 amu
   d. 36.46 amu
2. What is the molecular mass of each compound?
   a. 70.00 amu
   b. 153.81 amu
   c. 78.12 amu
   d. 80.06 amu
3. 180.17 amu
4. 386.73 amu
5. a. bent; polar
   b. trigonal planar; nonpolar
   c. bent; polar
6.
   a. pyramidal; polar
   b. bent; polar
   c. tetrahedral; nonpolar
7. linear; polar
8. linear; in a molecule with more than one central atom, the geometry around each central atom needs to be examined.

4.6: Organic Chemistry

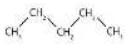
Concept Review Exercises

1. What is organic chemistry?
2. What is a functional group? Give at least two examples of functional groups.

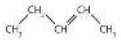
Answers

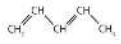
1. Organic chemistry is the study of the chemistry of carbon compounds.
2. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule; alcohol group and carboxylic group (answers will vary).

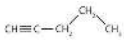
Exercises

1. Give three reasons why carbon is the central element in organic chemistry.
2. Are organic compounds based more on ionic bonding or covalent bonding? Explain.
3. Identify the type of hydrocarbon in each structure.
   a. 

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b. 

c. 

d. 

4. Identify the type of hydrocarbon in each structure.

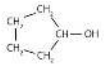
a. 

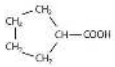
b. 

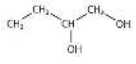
c.

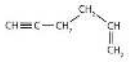
d. 

5. Identify the functional group(s) in each molecule.

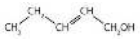
a. 

b. 

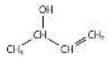
c. 

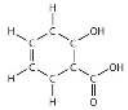
d. 

6. Identify the functional group(s) in each molecule.

a. 

b. 

c. 

d. 

7. How many functional groups described in this section contain carbon and hydrogen atoms only? Name them.

8. What is the difference in the ways the two oxygen atoms in the carboxyl group are bonded to the carbon atom?

Answers

1. 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).

2. Organic compounds are based on covalent bonding or electron sharing. The atoms C, H, O, N that make up organic compounds are all nonmetals.

3.

a. alkane
b. alkene
c. alkene
d. alkyne

4.

a. alkene
b. alkane
c. alkyne
d. alkene

5.

a. alcohol
b. carboxyl
c. alcohol
d. alkene and alkyne

6.

a. a carbon-carbon double bond and alcohol
b. carboxyl group
c. carbon-carbon double bond and alcohol
d. carbon-carbon double bond; alcohol and carboxyl group

7. two; carbon-carbon double bonds and carbon-carbon triple bonds

8. There are two oxygen atoms in a carboxyl group: one is double-bonded while the other is OH, single bonded to the same carbon atom.

Additional Exercises

Use the atomic masses found in Figure 2.7.1

1. An atomic mass unit equals 1.661×10^{-24} g. what is the mass in grams of each molecule of (a) H_2S (b) N_2O_4 (c) ICl_3 (d) NCl_3?
2. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of (a) O_2F_2 (b) CCl_4 (c) C_6H_6 (d) SO_3?
3. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of 5.00×10^{22} molecules of $C_9H_8O_4$?
4. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of 1.885×10^{20} molecules of $C_{27}H_{46}O$?
5. Acetic acid has the following structure:

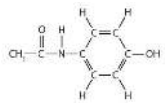


This molecule can lose a hydrogen ion (H^+) and the resulting anion can combine with other cations, such as Na^+:



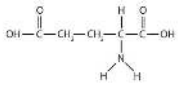
Name this ionic compound.

6. Formic acid (HCOOH) loses a hydrogen ion to make the formate ion ($HCOO^-$). Write the formula for each ionic compound: potassium formate, calcium formate, and ferric formate.
7. Cyanogen has the formula C_2N_2. Propose a bonding scheme that gives each atom the correct number of covalent bonds. (Hint: the two carbon atoms are in the center of a linear molecule.)
8. How many carbon–carbon single bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
9. How many carbon–carbon double bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
10. In addition to themselves, what other atoms can carbon atoms bond with and make covalent bonds that are nonpolar (or as nonpolar as possible)?
11. What is the greatest possible electronegativity difference between any two atoms? Use Figure 4.4 to find the answer.
12. Acetaminophen, a popular painkiller, has the following structure:



Name the recognizable functional groups in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

13. Glutamic acid is the parent compound of monosodium glutamate (known as MSG), which is used as a flavor enhancer. Glutamic acid has the following structure:



Name the functional groups you recognize in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

Answers

1.

a: 5.661×10^{-23} g

b: 1.528×10^{-22} g

c: 3.874×10^{-22} g

d: 1.999×10^{-22} g

2.

a: 1.163×10^{-22} g

b: 2.555×10^{-22} g

c: 1.298×10^{-22} g

d: 1.330×10^{-22} g

3. 14.96 g

4. 0.1211 g

5. sodium acetate

6.

a. KHCOO

b. $Ca(HCOO)_2$

c. $Fe(HCOO)_3$

7. :N≡C–C≡N:
8. 6.49×10^7 C-C bonds
9. 7.46×10^7 C=C bonds
10. Hydrogen atoms make relatively nonpolar bonds with carbon atoms.
11. The greatest electronegativity difference is 3.2, between F and Rb.
12. alcohol; the ring with double bonds, and the O=C-NH are also likely functional groups.
13. carboxyl and $-NH_2$ functional groups

Additional Questions

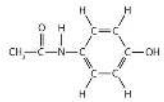
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5. Acetic acid has the following structure:



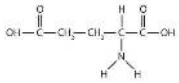
   This molecule can lose a hydrogen ion (H^+) and the resulting anion can combine with other cations, such as Na^+:



   Name this ionic compound.
6. Formic acid (HCOOH) loses a hydrogen ion to make the formate ion ($HCOO^-$). Write the formula for each ionic compound: potassium formate, calcium formate, and ferric formate.
7. Cyanogen has the formula C_2N_2. Propose a bonding scheme that gives each atom the correct number of covalent bonds. (Hint: the two carbon atoms are in the center of a linear molecule.)
8. The molecular formula C_3H_6 represents not only propene, a compound with a carbon–carbon double bond, but also a molecule that has all single bonds. Draw the molecule with formula C_3H_6 that has all single bonds.
9. How many carbon–carbon single bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
10. How many carbon–carbon double bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
11. In addition to themselves, what other atoms can carbon atoms bond with and make covalent bonds that are nonpolar (or as nonpolar as possible)?
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13. Acetaminophen, a popular painkiller, has the following structure:



   Name the recognizable functional groups in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?
14. Glutamic acid is the parent compound of monosodium glutamate (known as MSG), which is used as a flavor enhancer. Glutamic acid has the following structure:



   Name the functional groups you recognize in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

Answers

1. 1a: 5.75×10^{-23} g; 1b: 1.53×10^{-22} g; 1c: 3.88×10^{-22} g; 1d: 6.06×10^{-23} g

3. 14.96 g

5. sodium acetate

7. N≡C–C≡N

9. 6.49×10^7 bonds

11. Hydrogen atoms make relatively nonpolar bonds with carbon atoms.

13. alcohol; the N–H group, the ring with double bonds, and the C=O are also likely functional groups.

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4.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 mass of a molecule is called its **molecular mass** and is the sum of the masses of the atoms in the molecule. 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

5: 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.

5.0: Prelude to Introduction to Chemical Reactions
5.1: The Law of Conservation of Matter
5.2: Chemical Equations
5.3: Quantitative Relationships Based on Chemical Equations
5.4: Some Types of Chemical Reactions
5.5: Oxidation-Reduction (Redox) Reactions
5.6: Redox Reactions in Organic Chemistry and Biochemistry
5.E: Introduction to Chemical Reactions (Exercises)
5.S: Introduction to Chemical Reactions (Summary)

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5.0: Prelude to Introduction to Chemical Reactions

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are single-celled fungi. About 1,000 species are recognized, but the most common species is *Saccharomyces cerevisiae*, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

Yeasts live primarily on sugars, such as glucose ($C_6H_{12}O_6$). They convert glucose into carbon dioxide (CO_2) and ethanol (C_2H_5OH) in a chemical transformation that is represented as follows:

$$C_6H_{12}O_6\,(s) \longrightarrow 2\,CO_2\,(g) + 2\,C_2H_5OH(\ell)$$

Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of yeast, fermentation, depends on the production of ethanol, which results from the same chemical transformation. Some alcoholic beverages, such as champagne, can also be carbonated using the carbon dioxide produced by the yeast.

Yeast is among the simplest life forms on Earth, yet it is absolutely necessary for at least two major food industries. Without yeast to turn dough into bread and juice into wine, these foods and food industries would not exist today.

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5.1: The Law of Conservation of Matter

Learning Objectives

- Correctly define a law as it pertains to science.
- State the law of conservation of matter.

In science, a law is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge. One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is *conserved*.

With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist A. Lavoisier laid the foundation to the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. These eventually formed the basis of Dalton's Atomic Theory of Matter.

Law of Conservation of Mass

According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

$$\underbrace{\overbrace{\mathrm{HgO\,(s)}}^{\text{Mercuric oxide}}}_{100\ \mathrm{g}} \rightarrow \underbrace{\overbrace{\mathrm{Hg\,(l)}}^{\text{Mercury}}}_{92.6\ \mathrm{g}} + \underbrace{\overbrace{\mathrm{O_2\,(g)}}^{\text{Oxygen}}}_{7.4\ \mathrm{g}}$$

Another way of stating this is, "In a chemical reaction, matter is neither created nor destroyed." The law of conservation of mass is also known as the "law of indestructibility of matter."

Example 5.1.1

If heating 10 grams of $\mathrm{CaCO_3}$ produces 4.4 g of $\mathrm{CO_2}$ 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 (CaCO3). (Public Domain; Walkerma).

Solution

- Mass of the reactants, $\mathrm{CaCO_3}$: $10\,g$
- Mass of the products, $\mathrm{CO_2}$ 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.

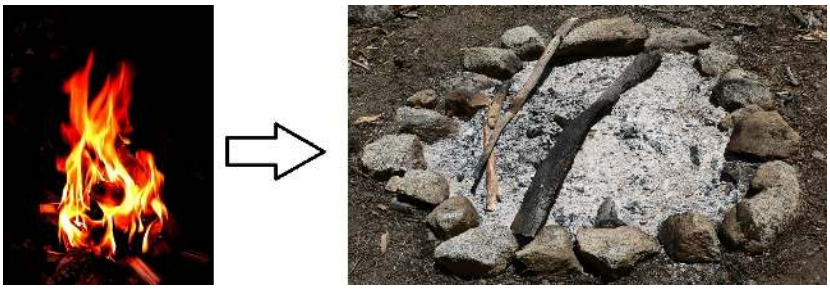


Figure 5.1.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

? Exercise 5.1.1

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

Answer a:

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

Answer b:

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

Key Takeaway

The amount of matter in a closed system is conserved.

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5.2: 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 5.2.1 shows a rather dramatic example of this very reaction.

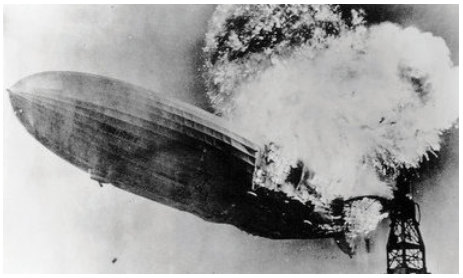


Figure 5.2.1: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin *SS Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

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:

$$H_2 + O_2 \rightarrow H_2O \tag{5.2.1}$$

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

$$H_2\,(g) + O_2\,(g) \rightarrow H_2O\ (\ell) \tag{5.2.2}$$

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 5.2.2).

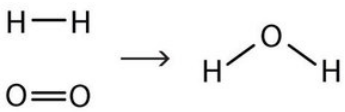


Figure 5.2.2: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.

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:

$$H_2\,(g) + O_2\,(g) \;\rightarrow 2\,H_2O\;(\ell) \tag{5.2.3}$$

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

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

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

$$2\,H_2\,(g) + O_2\,(g) \;\rightarrow 2\,H_2O\;(\ell) \tag{5.2.4}$$

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 5.2.3). The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

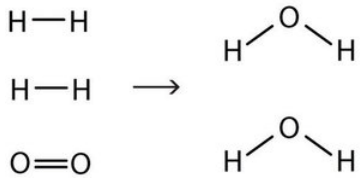


Figure 5.2.3: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.

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

✔ Example 5.2.1

Is each chemical equation balanced?

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

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 5.2.1

Is each chemical equation balanced?

a. $2\,Hg\,(l) + O_2\,(g) \longrightarrow Hg_2O_2\,(s)$
b. $C_2H_4\,(g) + 2\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(l)$
c. $Mg(NO_3)_2\,(s) + 2\,Li\,(s) \longrightarrow Mg\,(s) + 2\,LiNO_3\,(s)$.

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.

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

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

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

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

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

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

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{5.2.6}$$

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

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

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl \tag{5.2.7}$$

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

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

Example 5.2.2

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

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

$$Pb(NO_3)_2\,(aq) + NaCl\,(aq) \rightarrow NaNO_3\,(aq) + PbCl_2\,(s)$$

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

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

$$Pb(NO_3)_2\,(aq) + 2NaCl\,(aq) \rightarrow 2NaNO_3\,(aq) + PbCl_2\,(s)$$

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

Step 5: Think about the result.

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

Exercise 5.2.2

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



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

Answer

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

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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5.3: Quantitative Relationships Based on Chemical Equations

Learning Objectives

- To calculate the amount of one substance that will react with or be produced from a given amount of another substance.

A balanced chemical equation not only describes some of the chemical properties of substances—by showing us what substances react with what other substances to make what products—but also shows numerical relationships between the reactants and the products. The study of these numerical relationships is called stoichiometry. The stoichiometry of chemical equations revolves around the coefficients in the balanced chemical equation because these coefficients determine the molecular ratio in which reactants react and products are made.

> *The word stoichiometry is pronounced "stow-eh-key-OM-et-tree." It is of mixed Greek and English origins, meaning roughly "measure of an element."*

Looking Closer: Stoichiometry in Cooking

Let us consider a stoichiometry analogy from the kitchen. A recipe that makes 1 dozen biscuits needs 2 cups of flour, 1 egg, 4 tablespoons of shortening, 1 teaspoon of salt, 1 teaspoon of baking soda, and 1 cup of milk. If we were to write this as a chemical equation, we would write

$$\text{2 c flour + 1 egg + 4 tbsp shortening + 1 tsp salt + 1 tsp baking soda + 1 c milk} \rightarrow \text{12 biscuits}$$

(Unlike true chemical reactions, this one has all 1 coefficients written explicitly—partly because of the many different units here.) This equation gives us ratios of how much of what reactants are needed to make how much of what product. Two cups of flour, when combined with the proper amounts of the other ingredients, will yield 12 biscuits. One teaspoon of baking soda (when also combined with the right amounts of the other ingredients) will make 12 biscuits. One egg must be combined with 1 cup of milk to yield the product food. Other relationships can also be expressed.

We can use the ratios we derive from the equation for predictive purposes. For instance, if we have 4 cups of flour, how many biscuits can we make if we have enough of the other ingredients? It should be apparent that we can make a double recipe of 24 biscuits.

But how would we find this answer formally, that is, mathematically? We would set up a conversion factor, much like we did in Chapter 1. Because 2 cups of flour make 12 biscuits, we can set up an equivalency ratio:

$$\frac{\text{12 biscuits}}{\text{2 c flour}}$$

We then can use this ratio in a formal conversion of flour to biscuits:

$$\text{4 c flour} \times \frac{\text{12 biscuits}}{\text{2 c flour}} = \text{24 biscuits}$$

Similarly, by constructing similar ratios, we can determine how many biscuits we can make from any amount of ingredient. When you are doubling or halving a recipe, you are doing a type of stoichiometry. Applying these ideas to chemical reactions should not be difficult if you use recipes when you cook.



A recipe shows how much of each ingredient is needed for the proper reaction to take place. (CC BY-SA 3.0 Unported; Peng via Wikipedia)

Consider the following balanced chemical equation:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O \tag{5.3.1}$$

The coefficients on the chemical formulas give the ratios in which the reactants combine and the products form. Thus, we can make the following statements and construct the following ratios:

Table uses a statement from the balanced chemical reaction to show ratios and inverse ratios.

Statement from the Balanced Chemical Reaction	Ratio	Inverse Ratio
two C_2H_2 molecules react with five O_2 molecules	$\frac{2C_2H_2}{5O_2}$	$\frac{5O_2}{2C_2H_2}$
two C_2H_2 molecules react to make four CO_2 molecules	$\frac{2C_2H_2}{4CO_2}$	$\frac{4CO_2}{2C_2H_2}$
five O_2 molecules react to make two H_2O molecules	$\frac{5O_2}{2H_2O}$	$\frac{2H_2O}{5O_2}$
four CO_2 molecules are made at the same time as two H_2O molecules	$\frac{2H_2O}{4CO_2}$	$\frac{4CO_2}{2H_2O}$

Other relationships are possible; in fact, 12 different conversion factors can be constructed from this balanced chemical equation. In each ratio, the unit is assumed to be molecules because that is how we are interpreting the chemical equation.

Any of these fractions can be used as a conversion factor to relate an amount of one substance to an amount of another substance. For example, suppose we want to know how many CO_2 molecules are formed when 26 molecules of C_2H_2 are reacted. As usual with a conversion problem, we start with the amount we are given—$26C_2H_2$—and multiply it by a conversion factor that cancels out our original unit and introduces the unit we are converting to—in this case, CO_2. That conversion factor is $\frac{4CO_2}{2C_2H_2}$, which is composed of terms that come directly from the balanced chemical equation. Thus, we have

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2}$$

The molecules of C_2H_2 cancel, and we are left with molecules of CO_2. Multiplying through, we get

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2} = 52CO_2$$

Thus, 52 molecules of CO_2 are formed.

This application of stoichiometry is extremely powerful in its predictive ability, as long as we begin with a balanced chemical equation. Without a balanced chemical equation, the predictions made by simple stoichiometric calculations will be incorrect.

Example 5.3.1

Start with this balanced chemical equation.

$$KMnO_4 + 8\,HCl + 5\,FeCl_2 \longrightarrow 5\,FeCl_3 + MnCl_2 + 4\,H_2O + KCl$$

a. Verify that the equation is indeed balanced.
b. Give 2 ratios that give the relationship between HCl and $FeCl_3$.

Solution a

Each side has 1 K atom and 1 Mn atom. The 8 molecules of HCl yield 8 H atoms, and the 4 molecules of H_2O also yield 8 H atoms, so the H atoms are balanced. The Fe atoms are balanced, as we count 5 Fe atoms from 5 $FeCl_2$ reactants and 5 $FeCl_3$ products. As for Cl, on the reactant side, there are 8 Cl atoms from HCl and 10 Cl atoms from the 5 $FeCl_2$ formula units, for a total of 18 Cl atoms. On the product side, there are 15 Cl atoms from the 5 $FeCl_3$ formula units, 2 from the $MnCl_2$ formula unit, and 1 from the KCl formula unit. This is a total of 18 Cl atoms in the products, so the Cl atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.

Solution b

Because the balanced chemical equation tells us that 8 HCl molecules react to make 5 $FeCl_3$ formula units, we have the following 2 ratios: $\frac{8HCl}{5FeCl_3}$ and $\frac{5FeCl_3}{8HCl}$. There are a total of 42 possible ratios. Can you find the other 40 relationships?

Exercise 5.3.1

Start with this balanced chemical equation.

$$2KMnO_4 + 3CH_2{=}CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2CH_2OH + 2KOH$$

a. Verify that the equation is balanced.
b. Give 2 ratios that give the relationship between $KMnO_4$ and $CH_2{=}CH_2$. (A total of 30 relationships can be constructed from this chemical equation. Can you find the other 28?)

Answer a:

Each side has 2 K atoms and 2 Mn atoms. On the reactant side, 3 $CH_2{=}CH_2$ yield 6 C atoms and on the product side, 3 $HOCH_2CH_2OH$ also yield 6 C atoms, so the C atoms are balanced. There are 20 H atoms on the reactants side: 12 H atoms from 3 $CH_2{=}CH_2$ and 8 H atoms from 4 H_2O. On the product side, there are also 20 H atoms: 18 H atoms from 3 $HOCH_2CH_2OH$ and 2 H atoms from 2 KOH. So, the H atoms are balanced. As for O, on the reactant side, there are 8 O atoms from 2 $KMnO_4$ and 4 O atoms from 4 H_2O, for a total of 12 O atoms. On the product side, there are 4 O atoms from the 2 MnO_2 formula units, 6 O atoms from 3 $HOCH_2CH_2OH$, and 2 O atoms from the 2 KOH formula units. This is a total of 12 O atoms in the products, so the O atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.

Answer b:

Because the balanced chemical equation tells us that 2 $KMnO_4$ formula units react with 3 $CH_2{=}CH_2$ molecules, we have the following 2 ratios: $\frac{2KMnO_4}{3CH_2{=}CH_2}$ and $\frac{3CH_2{=}CH_2}{2KMnO_4}$. There are a total of 30 possible ratios. Can you find the other 28 relationships?

Key Takeaway

The coefficients in a balanced chemical equation give the ratios in which molecules of substances react and are produced in a chemical reaction.

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5.4: 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

$$4\,\mathrm{Fe} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{Fe_2O_3}$$

is a combination reaction that produces $\mathrm{Fe_2O_3}$ from its constituent elements — Fe and $\mathrm{O_2}$. Combination reactions do not have to combine elements, however. The chemical equation

$$\mathrm{Fe_2O_3} + 3\,\mathrm{SO_3} \rightarrow \mathrm{Fe_2(SO_4)_3}$$

shows a combination reaction in which $\mathrm{Fe_2O_3}$ combines with three molecules of $\mathrm{SO_3}$ to make $\mathrm{Fe_2(SO_4)_3}$.

Example 5.4.1

Which equations are combination reactions?

a. $\mathrm{Co\,(s) + Cl_2\,(g) \longrightarrow CoCl_2\,(s)}$
b. $\mathrm{CO\,(g) + Cl_2\,(g) \longrightarrow COCl_2\,(g)}$
c. $\mathrm{N_2H_4(\ell) + O_2\,(g) \longrightarrow N_2\,(g) + 2\,H_2O(\ell)}$

Solution

a. This is a combination reaction.
b. This is a combination reaction. (The compound $\mathrm{COCl_2}$ is called phosgene and, in the past, was used as a gassing agent in chemical warfare.)
c. This is not a combination reaction.

Exercise 5.4.1

Which equations are combination reactions?

a. $\mathrm{P_4\,(s) + 6\,Cl_2\,(g) \longrightarrow 4\,PCl_3\,(g)}$
b. $\mathrm{SO_3(\ell) + H_2O(\ell) \longrightarrow H_2SO_4(\ell)}$
c. $\mathrm{NaOH\,(s) + HCl\,(g) \longrightarrow NaCl\,(s) + H_2O(\ell)}$

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.

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$$

Another example is the burning of acetylene (C_2H_2) in welding torches:

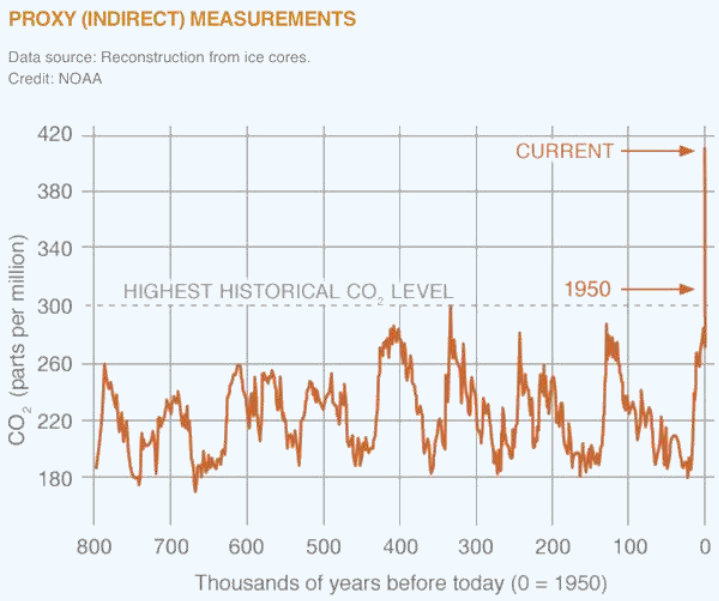
$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O$$

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 5.4.2

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

$$2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \longrightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g)$$

The balanced reaction argues that for every two molecules of octane that are burned, 16 molecules of CO_2 are generated.

Example 5.4.2

Identify each type of reaction.

a. $2\,K\,(s) + S\,(s) + 2\,O_2\,(g) \longrightarrow K_2SO_4\,(s)$
b. $(NH_4)_2Cr_2O_7\,(s) \longrightarrow N_2\,(g) + Cr_2O_3\,(s) + 4\,H_2O(\ell)$
c. $CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O(\ell)$

Solution

a. Multiple reactants are combining to make a single product, so this reaction is a combination reaction.
b. A single substance reacts to make several products, so we have a decomposition reaction.
c. 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 5.4.2

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

Key Takeaway

There are several recognizable types of chemical reactions: combination, decomposition, and combustion reactions are examples.

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5.5: 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 $5.5.1$):

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

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



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

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq) \longrightarrow H_2\,(g) + Zn^{2+}\,(aq) + 2\,Cl^-\,(aq)}$$

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 $\mathrm{Zn^{2+}}$. 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.

$$\begin{aligned} &Zn \rightarrow Zn^{2+} + \cancel{2e^-} \\ &\cancel{2H^+ + 2e^-} \rightarrow H_2 \\ \hline &Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \end{aligned}$$

Because we have two electrons on each side of the equation, they can be canceled. This is the key criterion for a balanced redox reaction: the electrons have to cancel exactly. If we check the charge on both sides of the equation, we see they are the same—2+. (In reality, this positive charge is balanced by the negative charges of the chloride ions, which are not included in this reaction because chlorine does not participate in the charge transfer.)

Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. **Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel**. The following example demonstrates this process.

Example 5.5.1: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Solution

We start by using symbols of the elements and ions to represent the reaction:

$$Ag^+ + Al \longrightarrow Ag + Al^{3+}$$

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:

$$\begin{aligned} &3\left(Ag^+ + e^- \rightarrow Ag\right) \\ &\underline{\qquad\qquad Al \rightarrow Al^{3+} + 3e^-} \\ &3Ag^+ + Al \rightarrow 3Ag + Al^{3+} \end{aligned}$$

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: $\mathrm{Ag^+}$

Exercise 5.5.1

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Answer

Reduction: $\mathrm{Ca^{2+} + 2\,e^- \longrightarrow Ca}$

Oxidation: \(2 \times (\ce{K -> K^{+} + e^{-}})\)

Combined: $\mathrm{Ca^{2+} + 2\,K \longrightarrow Ca + 2\,K^+}$

- The **substance oxidized** is the reactant that had undergone oxidation: K
- The **substance reduced** is the reactant that had undergone reduction: $\mathrm{Ca^{2+}}$
- The **reducing agent** is the same as the substance oxidized: K
- The **oxidizing agent** is the same as the substance reduced: $\mathrm{Ca^{2+}}$

Potassium has been used as a reducing agent to obtain various metals in their elemental form.

To Your Health: Redox Reactions and Pacemaker Batteries

All batteries use redox reactions to supply electricity because electricity is basically a stream of electrons being transferred from one substance to another. Pacemakers—surgically implanted devices for regulating a person's heartbeat—are powered by tiny batteries, so the proper operation of a pacemaker depends on a redox reaction.

Pacemakers used to be powered by NiCad batteries, in which nickel and cadmium (hence the name of the battery) react with water according to this redox reaction:

$$\mathrm{Cd\,(s) + 2\,NiOOH\,(s) + 2\,H_2O(\ell) \longrightarrow Cd(OH)_2\,(s) + 2\,Ni(OH)_2\,(s)}$$

The cadmium is oxidized, while the nickel atoms in NiOOH are reduced. Except for the water, all the substances in this reaction are solids, allowing NiCad batteries to be recharged hundreds of times before they stop operating. Unfortunately, NiCad batteries are fairly heavy batteries to be carrying around in a pacemaker. Today, the lighter lithium/iodine battery is used instead. The iodine is dissolved in a solid polymer support, and the overall redox reaction is as follows:

$$\mathrm{2\,Li\,(s) + I_2\,(s) \longrightarrow 2\,LiI\,(s)}$$

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 5.5.1: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of **oxidation** was "**adding oxygen**," so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for **reduction**: if a molecule

loses oxygen atoms, the molecule is being reduced. For example, the acetaldehyde (CH_3CHO) molecule takes on an oxygen atom to become acetic acid (CH_3COOH).

$$2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH$$

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 5.5.2

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 5.5.2

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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5.6: 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 5.6.1: 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. (CC BY-SA 2.0 Generic; Simon Law via Flickr).

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure 5.6.1).

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{5.6.1}$$

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 ($\mathrm{C_6H_{12}O_6}$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:

$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O} \tag{5.6.2}$$

Organic chemists use a variety of redox reactions. For example, potassium dichromate ($\mathrm{K_2Cr_2O_7}$) 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 ($\mathrm{CH_3CH_2OH}$) in a person's breath:

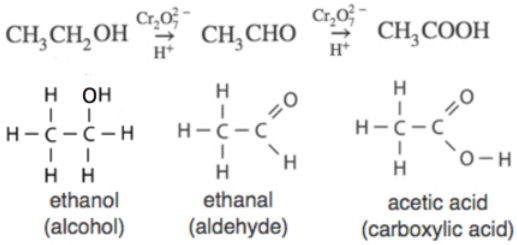
$$\mathrm{3\,CH_3CH_2OH + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O} \tag{5.6.3}$$

If the product acetaldehyde ($\mathrm{CH_3CHO}$) is not removed as it forms, it is further oxidized to acetic acid ($\mathrm{CH_3COOH}$). In this case, the overall reaction is as follows:

$$\mathrm{3\,CH_3CH_2OH + 2\,Cr_2O_7^{2-} + 16\,H^+ \rightarrow 3\,CH_3COOH + 4\,Cr^{3+} + 11\,H_2O} \tag{5.6.4}$$

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_3CH_2OH, a.k.a. ethanol) to form acetaldehayde (CH_3CHO, 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 ($CH_3CHOHCH_3$). It is the common solvent acetone [$(CH_3)_2CO$], which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:

$$3\,CH_3CHOHCH_3 + Cr_2O_7{}^{2-} + 8\,H^+ \rightarrow 3\,(CH_3)_2CO + 2\,Cr^{3+} + 7\,H_2O \tag{5.6.5}$$

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 ($CH_3COCOOH$) is reduced to lactic acid ($CH_3CHOHCOOH$) in the muscles.

$$CH_3COCOOH \rightarrow CH_3CHOHCOOH \tag{5.6.6}$$

(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):

$$C_6H_8O_6 + 2\,H^+ + 2\,NO_2{}^- \rightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO \tag{5.6.7}$$

> *If reaction in Equation 5.6.7 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 5.6.2).



Figure 5.6.2: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. (Pexels License; Scott Webb via Pexels)

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 5.6.3). The overall change that occurs is as follows:

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{5.6.8}$$

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 5.6.3: 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.

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5.E: Introduction to Chemical Reactions (Exercises)

5.1: The Law of Conservation of Matter

1. What is the law of conservation of matter?
2. How does the law of conservation of matter apply to chemistry?

ANSWERS

1. 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
2. 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.

Exercises

1. Express the law of conservation of matter in your own words.

2. Explain why the concept of conservation of matter is considered a scientific law.

3. Potassium hydroxide (KOH) readily reacts with carbon dioxide (CO_2) to produce potassium carbonate (K_2CO_3) and water (H_2O). How many grams of potassium carbonate is produced if 224.4 g of KOH reacted with 88.0 g of CO_2. The reaction also produced 36.0 g of water.

Answers

1. Matter may not be created or destroyed.

2. The concept is a scientific law because it is based on experimentation.

3. 276.4 g

5.2: Chemical Equations

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.

Exercises

1. Write a chemical equation to express the fact that hydrogen gas and solid iodine react to make gaseous hydrogen iodide. Make sure the equation satisfies the law of conservation of matter.
2. Write a chemical equation to express the fact that sodium metal and chlorine gas react to make solid sodium chloride. Make sure the equation satisfies the law of conservation of matter.
3. Write an equation expressing the fact that hydrogen gas and fluorine gas react to make gaseous hydrogen fluoride. Make sure the equation satisfies the law of conservation of matter.
4. Write an equation expressing the fact that solid potassium and fluorine gas react to make solid potassium fluoride. Make sure the equation satisfies the law of conservation of matter.
5. Mercury reacts with oxygen to make mercury(II) oxide. Write a balanced chemical equation that summarizes this reaction.

6. Octane (C_8H_{18}) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.
7. Propyl alcohol (C_3H_7OH) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.
8. Sulfuric acid (H_2SO_4) reacts with iron metal to make iron(III) sulfate and hydrogen gas. Write a balanced chemical equation that summarizes this reaction.
9. Balance each equation.
    a. $MgCl_2 + K \rightarrow KCl + Mg$
    b. $C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$
    c. $NaN_3 \rightarrow Na + N_2$ (This is the reaction used to inflate airbags in cars.)
10. Balance each equation.
    a. $NH_4NO_3 \rightarrow N_2O + H_2O$
    b. $TiBr_4 + H_2O \rightarrow TiO_2 + HBr$
    c. $C_3H_5N_3O_9 \rightarrow CO_2 + N_2 + O_2 + H_2O$ (This reaction represents the decomposition of nitroglycerine.)
11. Balance each equation.
    a. $NH_3 + O_2 \rightarrow NO + H_2O$
    b. $Li + N_2 \rightarrow Li_3N$
    c. $AuCl \rightarrow Au + AuCl_3$
12. Balance each equation.
    a. $NaOH + H_3PO_4 \rightarrow Na_3PO_4 + H_2O$
    b. $N_2H_4 + Cl_2 \rightarrow N_2 + HCl$
    c. $Na_2S + H_2S \rightarrow NaSH$
13. Chromium(III) oxide reacts with carbon tetrachloride to make chromium(III) chloride and phosgene ($COCl_2$). Write the balanced chemical equation for this reaction.
14. The reaction that occurs when an Alka-Seltzer tablet is dropped into a glass of water has sodium bicarbonate reacting with citric acid ($H_3C_6H_5O_7$) to make carbon dioxide, water, and sodium citrate ($Na_3C_6H_5O_7$). Write the balanced chemical equation for this reaction.
15. When sodium hydrogen carbonate is used to extinguish a kitchen fire, it decomposes into sodium carbonate, carbon dioxide and water. Write a balanced chemical equation for this reaction.
16. Elemental bromine gas can be generated by reacting sodium bromide with elemental chlorine. The other product is sodium chloride. Write a balanced chemical equation for this reaction.

Answers

1. $H_2(g) + I_2(s) \rightarrow 2HI(g)$
2. $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
3. $H_2(g) + F_2(g) \rightarrow 2HF(g)$
4. $2K(s) + F_2(g) \rightarrow 2KF(s)$
5. $2Hg + O_2 \rightarrow 2HgO$
6. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$
7. $2C_3H_7OH + 9O_2 \rightarrow 6CO_2 + 8H_2O$
8. $3H_2SO_4 + 2Fe \rightarrow Fe_2(SO_4)_3 + 3H_2$
9. a. $MgCl_2 + 2K \rightarrow 2KCl + Mg$

b. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
c. $2NaN_3 \rightarrow 2Na + 3N_2$

10.

a. $NH_4NO_3 \rightarrow N_2O + 2H_2O$
b. $TiBr_4 + 2H_2O \rightarrow TiO_2 + 4HBr$
c. $4C_3H_5N_3O_9 \rightarrow 12CO_2 + 6N_2 + O_2 + 10H_2O$

11.

a. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
b. $6Li + N_2 \rightarrow 2Li_3N$
c. $3AuCl \rightarrow 2Au + AuCl_3$

12.

a. $3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$
b. $N_2H_4 + 2Cl_2 \rightarrow N_2 + 4HCl$
c. $Na_2S + H_2S \rightarrow 2NaSH$

13. $Cr_2O_3 + 3CCl_4 \rightarrow 2CrCl_3 + 3COCl_2$

14. $3NaHCO_3 + H_3C_6H_5O_7 \rightarrow 3CO_2 + 3H_2O + Na_3C_6H_5O_7$

15. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

16. $2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$

5.3: Quantitative Relationships Based on Chemical Equations

Concept Review Exercises

1. Explain how stoichiometric ratios are constructed from a chemical equation.
2. Why is it necessary for a chemical equation to be balanced before it can be used to construct conversion factors?

Answers

1. Stoichiometric ratios are made using the coefficients of the substances in the balanced chemical equation.
2. A balanced chemical equation is necessary so one can construct the proper stoichiometric ratios.

Exercises

1. Balance this equation and write every stoichiometric ratio you can from it.

$$NH_4NO_3 \rightarrow N_2O + H_2O$$

2. Balance this equation.

$$N_2 + H_2 \rightarrow NH_3$$

3. Balance this equation and write every stoichiometric ratio you can from it.

$$Fe_2O_3 + C \rightarrow Fe + CO_2$$

4. Balance this equation.

$$Fe_2O_3 + CO \rightarrow Fe + CO_2$$

5. Balance this equation and determine how many molecules of CO_2 are formed if 15 molecules of C_6H_6 are reacted.

$$C_6H_6 + O_2 \rightarrow CO_2 + H_2O$$

6. Balance this equation and determine how many formula units of $Ag_2CO_3(s)$ are produced if 20 formula units of Na_2CO_3 are reacted.

$$Na_2CO_3(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + Ag_2CO_3(s)$$

7. Copper metal reacts with nitric acid according to this equation:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(\ell)$$

   a. Verify that this equation is balanced.
   b. How many Cu atoms will react if 488 molecules of aqueous HNO_3 are reacted?

8. Gold metal reacts with a combination of nitric acid and hydrochloric acid according to this equation:

$$Au(s) + 3HNO_3(aq) + 4HCl(aq) \rightarrow HAuCl_4(aq) + 3NO_2(g) + 3H_2O(\ell)$$

   a. Verify that this equation is balanced.
   b. How many Au atoms react with 639 molecules of aqueous HNO_3?

9. Sulfur can be formed by reacting sulfur dioxide with hydrogen sulfide at high temperatures according to this equation:

$$SO_2(g) + 2H_2S(g) \rightarrow 3S(g) + 2H_2O(g)$$

   a. Verify that this equation is balanced.
   b. How many S atoms will be formed from by reacting 1,078 molecules of H_2S?

10. Nitric acid is made by reacting nitrogen dioxide with water:

$$3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g)$$

   a. Verify that this equation is balanced.
   b. How many molecules of NO will be formed by reacting 2,268 molecules of NO_2?

Answers

1. $NH_4NO_3 \rightarrow N_2O + 2H_2O$; the stoichiometric ratios are $\frac{1NH_4NO_3}{1N_2O}$, $\frac{1NH_4NO_3}{2H_2O}$, $\frac{1N_2O}{2H_2O}$, and their reciprocals.
2. $N_2 + 3H_2 \rightarrow 2NH_3$
3. $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$; the stoichiometric ratios are $\frac{2Fe_2O_3}{3C}$, $\frac{2Fe_2O_3}{4Fe}$, $\frac{2Fe_2O_3}{3CO_2}$, $\frac{3C}{4Fe}$, $\frac{3C}{3CO_2}$, $\frac{4Fe}{3CO_2}$, and their reciprocals.
4. $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
5. $2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$; 90 molecules
6. $Na_2CO_3(aq) + 2AgNO_3(aq) \rightarrow 2NaNO_3(aq) + Ag_2CO_3(s)$; 20 formula units
7.
   a. It is balanced.
   b. 183 atoms
8.
   a. It is balanced.
   b. 213 atoms
9.
   a. It is balanced.
   b. 1,617 atoms
10.
   a. It is balanced.
   b. 756 molecules

5.4: Some Types of Chemical Reactions

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.

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. $3O_2(g) \rightarrow 2O_3(g)$

Answers

1.

    a. combustion

    b. decomposition

    c. combination

2.

    a. combination

    b. combination

    c. decomposition

3.

    a. decomposition

    b. combustion (also combination)

    c. combination

4.

a. combination

b. decomposition

c. combination

5.5: Oxidation-Reduction (Redox) Reactions

Concept Review Exercises

1. Give two different definitions for oxidation and reduction.
2. Give an example of each definition of oxidation and reduction.

Answers

1. Oxidation is the loss of electrons or the addition of oxygen; reduction is the gain of electrons or the addition of hydrogen.
2. $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation); $C_2H_4 + H_2 \rightarrow C_2H_6$ (reduction) (answers will vary)

Exercises

1. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.

   a. $NaOH + HCl \rightarrow H_2O + NaCl$
   b. $3Mg + 2AlCl_3 \rightarrow 2Al + 3MgCl_2$
   c. $H_2O_2 + H_2 \rightarrow 2H_2O$
   d. $KCl + AgNO_3 \rightarrow AgCl + KNO_3$

2. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.

   a. $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
   b. $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$
   c. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
   d. $2K + 2H_2O \rightarrow 2KOH + H_2$

3. Balance each redox reaction by writing appropriate half reactions and combining them to cancel the electrons.

   a. $Ca(s) + H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$
   b. $I^-(aq) + Br_2(\ell) \rightarrow Br^-(aq) + I_2(s)$

4. Balance each redox reaction by writing appropriate half reactions and combining them to cancel the electrons.

   a. $Fe(s) + Sn^{4+}(aq) \rightarrow Fe^{3+}(aq) + Sn^{2+}(aq)$
   b. $Pb(s) + Pb^{4+}(aq) \rightarrow Pb^{2+}(aq)$ (Hint: both half reactions will yield the same product.)

Answers

1.

   a. no

   b. yes; oxidizing agent: $AlCl_3$; reducing agent: Mg

   c. yes; oxidizing agent: H_2O_2; reducing agent: H_2

   d. no

2.

   a. yes; oxidizing agent: HNO_3; reducing agent: Cu
   b. yes; oxidizing agent: O_2; reducing agent: C_2H_6
   c. no

d. yes; oxidizing agent: H_2O; reducing agent: K

3.

a. Combined: $Ca + 2H^+ \rightarrow Ca^{2+} + H_2$
b. Combined: $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

4.

a. $(Fe \rightarrow Fe^{3+} + 3e^-) \times 2$

$(Sn^{4+} + 2e^- \rightarrow Sn^{2+}) \times 3$

Combined: $2Fe + 3Sn^{4+} \rightarrow 2Fe^{3+} + 3Sn^{2+}$

b. $Pb \rightarrow Pb^{2+} + 2e^-$

$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$

Combined: $Pb + Pb^{4+} \rightarrow 2Pb^{2+}$

5.6: Redox Reactions in Organic Chemistry and Biochemistry

Concept Review Exercise

1. Give some biochemical examples of oxidation and reduction reactions.

Answer

1. photosynthesis and antioxidants in foods (answers will vary)

Exercises

1. A typical respiratory reaction discussed in the text is the oxidation of glucose ($C_6H_{12}O_6$):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

Is this a redox reaction? If so, what are the oxidizing and reducing agents?

2. The major net reaction in photosynthesis is as follows:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Is this a redox reaction? If so, what are the oxidizing and reducing agents?

3. What would be the ultimate organic product if $CH_3CH_2CH_2OH$ were to react with a solution of $K_2Cr_2O_7$?
4. What would be the ultimate organic product if $CH_3CH_2CH_2CH_2OH$ were to react with a solution of $K_2Cr_2O_7$?
5. What would be the final organic product if $CH_3CH_2CHOHCH_3$ were to react with a solution of $K_2Cr_2O_7$?
6. What would be the major organic product if $CH_3CH_2CHOHCH_2CH_3$ were to react with a solution of $K_2Cr_2O_7$?
7. What alcohol is produced in the reduction of acetone [$(CH_3)_2CO$]?
8. What alcohol is produced in the reduction of propanal (CH_3CH_2CHO)?

Answers

1. yes; oxidizing agent: O_2; reducing agent: $C_6H_{12}O_6$
2. yes; oxidizing agent: CO_2; reducing agent: H_2O
3. CH_3CH_2COOH
4. $CH_3CH_2CH_2COOH$
5. $CH_3CH_2C(O)CH_3$, where the carbon is double bonded to the oxygen
6. $CH_3CH_2C(O)CH_2CH_3$, carbon #3 is double bonded to the oxygen

7. $CH_3CHOHCH_3$, or isopropyl alcohol

8. $CH_3CH_2CH_2OH$

5.

Additional Exercises

1. Isooctane (C_8H_{18}) is used as a standard for comparing gasoline performance. Write a balanced chemical equation for the combustion of isooctane.
2. Heptane (C_7H_{16}), like isooctane (see Exercise 1), is also used as a standard for determining gasoline performance. Write a balanced chemical equation for the combustion of heptane.
3. What is the difference between a combination reaction and a redox reaction? Are all combination reactions also redox reactions? Are all redox reactions also combination reactions?
4. Are combustion reactions always redox reactions as well? Explain.
5. A friend argues that the equation

   $$Fe^{2+} + Na \rightarrow Fe + Na^{+}$$

   is balanced because each side has one iron atom and one sodium atom. Explain why your friend is incorrect.
6. Some antacids contain aluminum hydroxide [$Al(OH)_3$]. This compound reacts with excess hydrochloric acid (HCl) in the stomach to neutralize it. If the products of this reaction are water and aluminum chloride, what is the balanced chemical equation for this reaction? What is the stoichiometric ratio between the number of HCl molecules made to the number of H_2O molecules made?
7. Sulfuric acid is made in a three-step process: (1) the combustion of elemental sulfur to produce sulfur dioxide, (2) the continued reaction of sulfur dioxide with oxygen to produce sulfur trioxide, and (3) the reaction of sulfur trioxide with water to make sulfuric acid (H_2SO_4). Write balanced chemical equations for all three reactions.
8. If the products of glucose metabolism are carbon dioxide and water, what is the balanced chemical equation for the overall process? What is the stoichiometric ratio between the number of CO_2 molecules made to the number of H_2O molecules made?
9. Historically, the first true battery was the Leclanché cell, named after its discoverer, Georges Leclanché. It was based on the following reaction:

   $$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

   Identify what is being oxidized, what is being reduced, and the respective reducing and oxidizing agents.

Answers

1. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

2. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

3. A combination reaction makes a new substance from more than one reactant; a redox reaction rearranges electrons. Most (not all) combination reactions are redox reactions. Not all redox reactions are combination reactions.

4. All combustion reactions are redox reactions. In combustion a chemical is combining with oxygen and that chemical is being oxidized. Oxygen, on the other hand, is being reduced.

5. Your friend is incorrect because the number of electrons transferring is not balanced. A balanced equation must not only have the same number of atoms of each element on each side of the equation but must also have the same charge on both sides.

6. $Al(OH)_3 + 3HCl \rightarrow 3H_2O + AlCl_3$; 1:1

7. (1) $S + O_2 \rightarrow SO_2$; (2) $2SO_2 + O_2 \rightarrow 2SO_3$; (3) $SO_3 + H_2O \rightarrow H_2SO_4$

8. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$; 1:1

9. oxidized and reducing agent: Zn; reduced and oxidizing agent: Cu^{2+}

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5.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

6: 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.

6.0: Prelude to Quantities in Chemical Reactions
6.1: The Mole and Avogadro's Number
6.2: Gram-Mole Conversions
6.3: Mole Relationships in Chemical Reactions
6.4: Mass Relationships and Chemical Equations
6.5: Limiting Reagent and Percent Yield
6.E: Quantities in Chemical Reactions (Exercise)
6.S: Quantities in Chemical Reactions (Summary)

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6.0: 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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6.1: The Mole and Avogadro's Number

Learning Objectives

- Define the amount unit mole and the related quantity Avogadro's number.
- Calculate molar mass of a compound from the molecular formula.

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

The Mole

So far, we have been talking about chemical substances in terms of individual atoms and molecules. Yet we do not typically deal with substances one atom or molecule at a time; we work with millions, billions, and trillions of atoms and molecules at a time. We need a way to deal with macroscopic, rather than microscopic, amounts of matter. We need a unit of amount that relates quantities of substances on a scale that we can interact with.

Chemistry uses a unit called **mole**. The mole (mol) is an counting term similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. A mole is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word "mole" is "large mass" or "bulk," which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

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

How big is a mole? It is very large. Suppose you had a mole of dollar bills that need to be counted. If everyone on earth (about 6 billion people) counted one bill per second, it would take about 3.2 million years to count all the bills. A mole of sand would fill a cube about 32 km on a side. A mole of pennies stacked on top of each other would have about the same diameter as our galaxy, the Milky Way. Atoms and molecules are very tiny, so one mole of carbon atoms would make a cube that is 1.74 cm on a side, small enough to carry in your pocket. One mole of water molecules is approximately 18 mL or just under 4 teaspoons of water.

Example 6.1.3

How many molecules are present in 2.76 mol of H_2O? How many atoms is this?

Solution

The definition of a mole is an equality that can be used to construct a conversion factor. Also, because we know that there are three atoms in each molecule of H_2O, we can also determine the number of atoms in the sample.

$$2.76\ \cancel{mol\ H_2O} \times \frac{6.022 \times 10^{23} molecules\ H_2O}{\cancel{mol\ H_2O}} = 1.66 \times 10^{24} molecules\ H_2O$$

To determine the total number of atoms, we have

$$1.66 \times 10^{24}\ \cancel{molecules\ H_2O} \times \frac{3\ atoms}{1\ molecule} = 4.99 \times 10^{24}\ atoms$$

? Exercise 6.1.3

How many molecules are present in 4.61×10^{-2} mol of O_2?

Answer

2.78×10^{22} molecules

Molar Mass

Why is the mole unit so important? It represents the link between the microscopic and the macroscopic, especially in terms of mass. *A mole of a substance has the same mass in grams as one unit (atom or molecules) has in atomic mass units*. The mole unit allows us to express amounts of atoms and molecules in visible amounts that we can understand.

For example, we already know that, by definition, a mole of carbon has a mass of exactly 12 g. This means that exactly 12 g of C has 6.022×10^{23} atoms:

$$12 \text{ g C} = 6.022 \times 10^{23} \text{ atoms C}$$

We can use this equality as a conversion factor between the number of atoms of carbon and the number of grams of carbon. How many grams are there, say, in 1.50×10^{25} atoms of carbon? This is a one-step conversion:

$$1.50 \times 10^{25} \cancel{atoms\,C} \times \frac{12.0000\,g\,C}{6.022 \times 10^{23} \cancel{atoms\,C}} = 299\,g\,C$$

But it also goes beyond carbon. Previously we defined atomic and molecular masses as the number of atomic mass units per atom or molecule. Now we can do so in terms of grams. The atomic mass of an element is the number of grams in 1 mol of atoms of that element, while the molecular mass of a compound is the number of grams in 1 mol of molecules of that compound. Sometimes these masses are called **molar masses** to emphasize the fact that they are the mass for 1 mol of things. (The term *molar* is the adjective form of mole and has nothing to do with teeth.)

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (Figure 6.1.1).

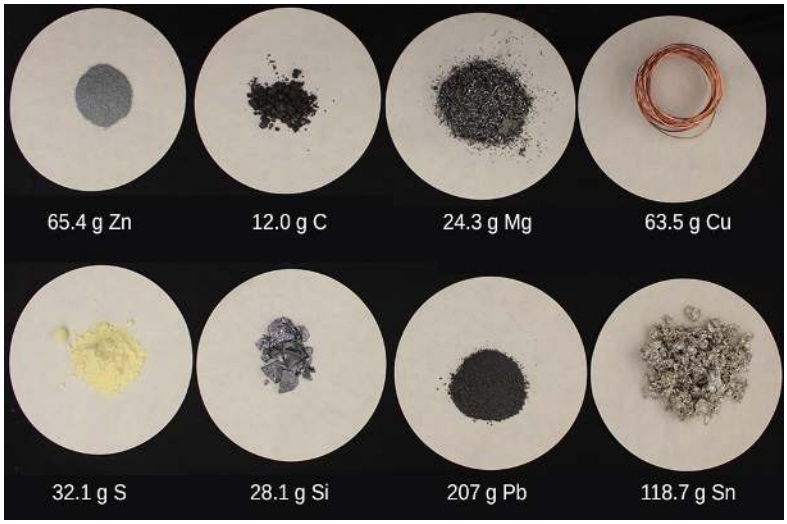


Figure 6.1.1: Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

This figure contains eight different substances displayed on white circles. The amount of each substance is visibly different.

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs

12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C.

Table 6.1.1: Mass of one mole of elements

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

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water after a rainfall. Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.



Video 6.1.1: The mole is used in chemistry to represent 6.022×10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this video and then complete the “Think” questions that follow. Explore more about the mole by reviewing the information under “Dig Deeper.”

The relationships between formula mass, the mole, and Avogadro’s number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance’s mass.

Here are some examples. The mass of 1 hydrogen atom is 1.0079 u; the mass of 1 mol of hydrogen atoms is 1.0079 g. Elemental hydrogen exists as a diatomic molecule, H_2. One molecule has a mass of 1.0079 u + 1.0079 u = 2.0158 u, while 1 mol of H_2 has a mass of 1.0079 g + 1.0079 g = 2.0158 g. One molecule of H_2O has a mass of about 18.01 u; 1 mol H_2O has a mass of 18.01 g. A single unit of NaCl has a mass of 58.45 u; NaCl has a molar mass of 58.45 g. In each of these moles of substances, there are 6.022×10^{23} units: 6.022×10^{23} atoms of H, 6.022×10^{23} molecules of H_2 and H_2O, 6.022×10^{23} units of NaCl ions. These relationships give us plenty of opportunities to construct conversion factors for simple calculations.

Example 6.1.4: Sugar

What is the molar mass of sugar ($C_6H_{12}O_6$)?

Solution

To determine the molar mass, we simply add the atomic masses of the atoms in the molecular formula; but express the total in grams per mole, not atomic mass units. The masses of the atoms can be taken from the periodic table.

6 C = 6 × 12.011	= 72.066
12 H = 12 × 1.0079	= 12.0948
6 O = 6 × 15.999	= 95.994
TOTAL	= 180.155 g/mol

Per convention, the unit *grams per mole* is written as a fraction.

Exercise 6.1.4

What is the molar mass of $AgNO_3$?

Answer

169.87 g/mol

Summary

The mole is a key unit in chemistry. The molar mass of a substance, in grams, is numerically equal to one atom's or molecule's mass in atomic mass units.

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6.2: Gram-Mole Conversions

Learning Objectives

- To convert between mass units and mole units.

As we just discussed, **molar mass** is defined as the mass (in grams) of 1 mole of substance (or Avogadro's number of molecules or formula units).

The simplest type of manipulation using molar mass as a *conversion factor* is a mole-gram conversion (or its reverse, a gram-mole conversion).

We also established that 1 mol of Al has a mass of 26.98 g (Example 6.2.1). Stated mathematically,

$$1 \text{ mol Al} = 26.98 \text{ g Al}$$

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \quad \text{and} \quad \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

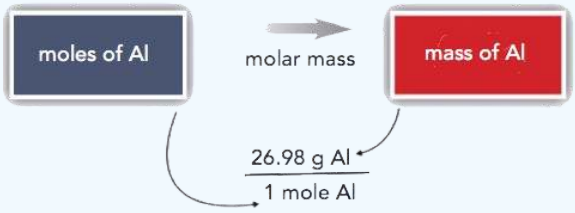
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

Example 6.2.1

What is the mass of 3.987 mol of Al?

Solution

The first step in a conversion problem is to decide what conversion factor to use. Because we are starting with mole units, we want a conversion factor that will cancel the mole unit and introduce the unit for mass in the numerator. Therefore, we should use the $\frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$ conversion factor. We start with the given quantity and multiply by the conversion factor:



$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

Note that the mol units cancel algebraically. (The quantity 3.987 mol is understood to be in the numerator of a fraction that has 1 in the unwritten denominator.) Canceling and solving gives

$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 107.6 \text{ g Al}$$

Our final answer is expressed to four significant figures.

Exercise 6.2.1

How many moles are present in 100.0 g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

Answer

$$100.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 3.706 \text{ mol Al}$$

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure 6.2.1 is a chart for determining what conversion factor is needed, and Figure 6.2.2 is a flow diagram for the steps needed to perform a conversion.

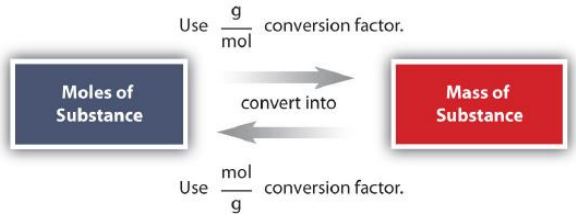


Figure 6.2.1 A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

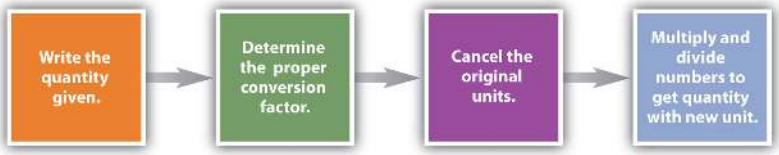


Figure 6.2.2 A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

Example 6.2.2

A biochemist needs 0.00655 mol of bilirubin ($C_{33}H_{36}N_4O_6$) for an experiment. How many grams of bilirubin will that be?

Solution

To convert from moles to mass, we need the molar mass of bilirubin, which we can determine from its chemical formula:

33 C molar mass:	33 × 12.01 g =	396.33 g
36 H molar mass:	36 × 1.01 g =	36.36 g
4 N molar mass:	4 × 14.01 g =	56.04 g
6 O molar mass:	6 × 16.00 g =	96.00 g
Total:		584.73 g

The molar mass of bilirubin is 584.73 g. Using the relationship

$$1 \text{ mol bilirubin} = 584.73 \text{ g bilirubin}$$

we can construct the appropriate conversion factor for determining how many grams there are in 0.00655 mol. Following the steps from Figure 6.2.2:

$$0.00655 \text{ mol bilirubin} \times \frac{584.73 \text{ g bilirubin}}{\text{mol bilirubin}} = 3.83 \text{ g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

Exercise 6.2.2

A chemist needs 457.8 g of $KMnO_4$ to make a solution. How many moles of $KMnO_4$ is that?

Answer

$$457.8 \text{ g } KMnO_4 \times \frac{1 \text{ mol } KMnO_4}{158.04 \text{ g } KMnO_4} = 2.897 \text{ mol } KMnO_4$$

To Your Health: Minerals

For our bodies to function properly, we need to ingest certain substances from our diets. Among our dietary needs are minerals, the noncarbon elements our body uses for a variety of functions, such developing bone or ensuring proper nerve transmission. The US Department of Agriculture has established some recommendations for the RDIs of various minerals. The accompanying table lists the RDIs for minerals, both in mass and moles, assuming a 2,000-calorie daily diet.

Table 6.2.1: Essential Minerals and their Composition in Humans

Mineral	Male (age 19–30 y)		Female (age 19–30 y)	
Ca	1,000 mg	0.025 mol	1,000 mg	0.025 mol
Cr	35 µg	6.7×10^{-7} mol	25 µg	4.8×10^{-7} mol
Cu	900 µg	1.4×10^{-5} mol	900 µg	1.4×10^{-5} mol
F	4 mg	2.1×10^{-4} mol	3 mg	1.5×10^{-4} mol
I	150 µg	1.2×10^{-6} mol	150 µg	1.2×10^{-6} mol
Fe	8 mg	1.4×10^{-4} mol	18 mg	3.2×10^{-4} mol
K	3,500 mg	9.0×10^{-2} mol	3,500 mg	9.0×10^{-2} mol
Mg	400 mg	1.6×10^{-2} mol	310 mg	1.3×10^{-2} mol
Mn	2.3 mg	4.2×10^{-5} mol	1.8 mg	3.3×10^{-5} mol
Mo	45 mg	4.7×10^{-7} mol	45 mg	4.7×10^{-7} mol
Na	2,400 mg	1.0×10^{-1} mol	2,400 mg	1.0×10^{-1} mol
P	700 mg	2.3×10^{-2} mol	700 mg	2.3×10^{-2} mol
Se	55 µg	7.0×10^{-7} mol	55 µg	7.0×10^{-7} mol
Zn	11 mg	1.7×10^{-4} mol	8 mg	1.2×10^{-4} mol

Table 6.2.1 illustrates several things. First, the needs of men and women for some minerals are different. The extreme case is for iron; women need over twice as much as men do. In all other cases where there is a different RDI, men need more than women.

Second, the amounts of the various minerals needed on a daily basis vary widely—both on a mass scale and a molar scale. The average person needs 0.1 mol of Na a day, which is about 2.5 g. On the other hand, a person needs only about 25–35 µg of Cr per day, which is under one millionth of a mole. As small as this amount is, a deficiency of chromium in the diet can lead to diabetes-like symptoms or neurological problems, especially in the extremities (hands and feet). For some minerals, the body does not require much to keep itself operating properly.

Although a properly balanced diet will provide all the necessary minerals, some people take dietary supplements. However, too much of a good thing, even minerals, is not good. Exposure to too much chromium, for example, causes a skin irritation, and certain forms of chromium are known to cause cancer (as presented in the movie *Erin Brockovich*).

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6.3: Mole Relationships 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:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$

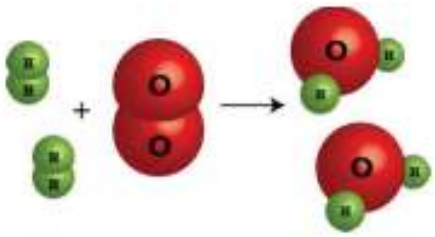
These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ \text{mol}\ \ H_2 + 1\ \ \text{mol}\ \ O_2 \longrightarrow 2\ \text{mol}\ \ H_2O$$

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 6.3.1: This representation of the production of water from oxygen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

By the same token, the ratios we constructed to describe molecules reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following

ratios:

$$\frac{2\text{ mol }H_2}{1\text{ mol }O_2}\text{ or }\frac{1\text{ mol }O_2}{2\text{ mol }H_2}$$

$$\frac{2\text{ mol }H_2O}{1\text{ mol }O_2}\text{ or }\frac{1\text{ mol }O_2}{2\text{ mol }H_2O}$$

$$\frac{2\text{ mol }H_2}{2\text{ mol }H_2O}\text{ or }\frac{2\text{ mol }H_2O}{2\text{ mol }H_2}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called ***stoichiometry*****.** The ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products is called the **stoichiometric factor.**

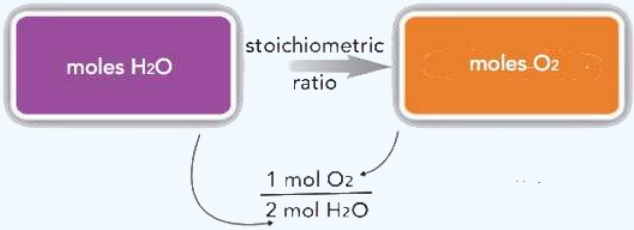
✔ Example 6.3.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O? The balanced equation is as follows:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Solution

Because we are dealing with quantities of H_2O and O_2, we will use the **stoichiometric ratio** that relates those two substances. Because we are given an amount of H_2O and want to determine an amount of O_2, we will use the ratio that has H_2O in the denominator (so it cancels) and O_2 in the numerator (so it is introduced in the answer). Thus,



$$27.6\text{ mol }H_2O \times \frac{1\text{ mol }O_2}{2\text{ mol }H_2O} = 13.8\text{ mol }O_2$$

To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.

? Exercise 6.3.1

Using $2H_2 + O_2 \rightarrow 2H_2O$, how many moles of hydrogen react with 3.07 mol of oxygen to produce H_2O?

Answer

$$3.07\text{ mol }O_2 \times \frac{2\text{ mol }H_2}{1\text{ mol }O_2} = 6.14\text{ mol }H_2$$

Key Takeaway

- The balanced chemical reaction can be used to determine molar relationships between substances.

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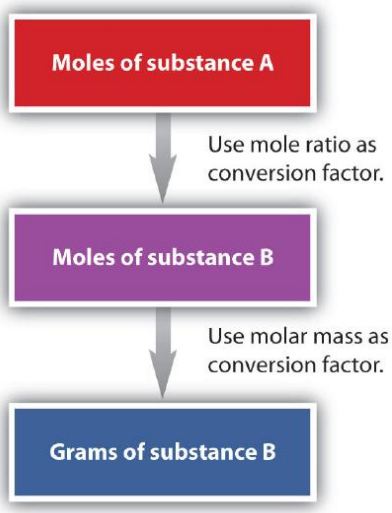
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6.4: Mass Relationships and Chemical Equations

Learning Objectives

- To convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

$$Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3$$

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:

$$3.59\ \text{mol}\ Fe_2O_3 \times \frac{3\ \text{mol}\ SO_3}{1\ \text{mol}\ Fe_2O_3} = 10.77\ \text{mol}\ SO_3$$

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:

$$10.77\ \text{mol}\ SO_3 \times \frac{80.07\ \text{g}\ SO_3}{1\ \text{mol}\ SO_3} = 862.4\ \text{g}\ SO_3$$

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 6.4.1

How many grams of CO_2 are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation?

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Solution

Our strategy will be to convert from moles of HCl to moles of CO_2 and then from moles of CO_2 to grams of CO_2. We will need the molar mass of CO_2, which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of CO_2:

$$2.09 \text{ mol HCl} \times \underbrace{\frac{1 \text{ mol } CO_2}{2 \text{ mol HCl}}}_{\text{from the coefficients of the balanced equation}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 46.0 \text{ g } CO_2$$

The molar ratio between CO_2 and HCl comes from the balanced chemical equation.

Exercise

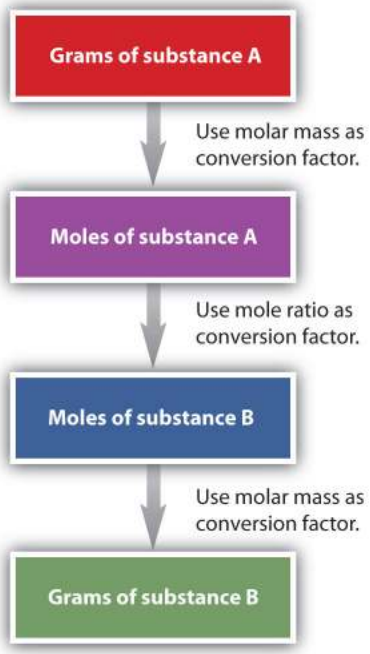
How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of H_2O are reacted according to this balanced chemical equation?

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2$$

Answer

$$17.3 \text{ mol } H_2O \times \frac{1 \text{ mol } C_6H_{12}O_6}{6 \text{ mol } H_2O} \times \frac{180.18 \text{ g } C_6H_{12}O_6}{1 \text{ mol } C_6H_{12}O_6} = 520 \text{ g } C_6H_{12}O_6$$

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:



This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques.

Example 6.4.2: Chlorination of Carbon

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

How many grams of HCl are produced by the reaction of 100.0 g of CH_4?

Solution

First, let us work the problem in stepwise fashion. We begin by converting the mass of CH_4 to moles of CH_4, using the molar mass of CH_4 (16.05 g/mol) as the conversion factor:

$$100.0\text{ g } CH_4 \times \frac{1\text{ mol } CH_4}{16.05\text{ g } CH_4} = 6.231\text{ mol } CH_4$$

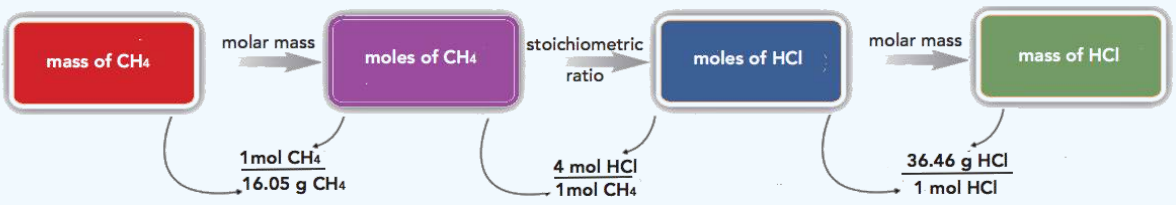
Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles CCl_4 and moles HCl and convert our first result into moles of HCl:

$$6.231\text{ mol } CH_4 \times \frac{4\text{ mol HCl}}{1\text{ mol } CH_4} = 24.92\text{ mol HCl}$$

Finally, we use the molar mass of HCl (36.46 g/mol) as a conversion factor to calculate the mass of 24.92 mol of HCl:

$$24.92\text{ mol HCl} \times \frac{36.46\text{ g HCl}}{1\text{ mol HCl}} = 908.5\text{ g HCl}$$

In each step, we have limited the answer to the proper number of significant figures. If desired, we can do all three conversions on a single line:



$$100.0\ \text{g CH}_4 \times \frac{1\ \text{mol CH}_4}{16.05\ \text{g CH}_4} \times \frac{4\ \text{mol HCl}}{1\ \text{mol CH}_4} \times \frac{36.46\ \text{g HCl}}{1\ \text{mol HCl}} = 908.7\ \text{g HCl}$$

This final answer is slightly different from our first answer because only the final answer is restricted to the proper number of significant figures. In the first answer, we limited each intermediate quantity to the proper number of significant figures. As you can see, both answers are essentially the same.

? Exercise 6.4.2: Oxidation of Propanal

The oxidation of propanal (CH_3CH_2CHO) to propionic acid (CH_3CH_2COOH) has the following chemical equation:

$$CH_3CH_2CHO + 2K_2Cr_2O_7 \rightarrow CH_3CH_2COOH + \text{other products}$$

How many grams of propionic acid are produced by the reaction of 135.8 g of $K_2Cr_2O_7$?

Answer

$$135.8\ \text{g } K_2Cr_2O_7 \times \frac{1\ \text{mol } K_2Cr_2O_7}{294.20\ \text{g } K_2Cr_2O_7} \times \frac{1\ \text{mol } CH_3CH_2COOH}{2\ \text{mol } K_2Cr_2O_7} \times \frac{74.09\ \text{g } CH_3CH_2COOH}{1\ \text{mol } CH_3CH_2COOH} = 17.10\ \text{g } CH_3CH_2COOH$$

To Your Health: The Synthesis of Taxol

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

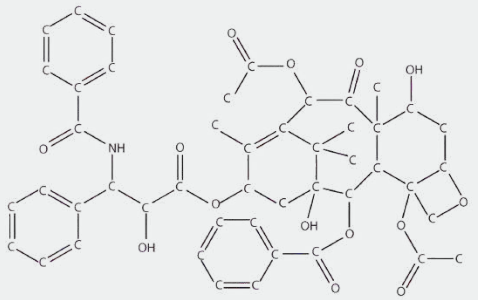


Figure 6.4.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

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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6.5: Limiting Reagent and Percent Yield

Learning Objectives

- Define and determine theoretical yields, actual yields, and percent yields.
- Identify a limiting reagent from a set of reactants.
- Calculate how much product will be produced from the limiting reagent.
- Calculate how much reactant(s) remains when the reaction is complete.

Yield

In all the previous calculations we have performed involving balanced chemical equations, we made two assumptions:

1. The reaction goes exactly as written.
2. The reaction proceeds completely.

In reality, such things as side reactions occur that make some chemical reactions rather messy. For example, in the actual combustion of some carbon-containing compounds, such as methane, some CO is produced as well as CO_2. However, we will continue to ignore side reactions, unless otherwise noted. The second assumption, that the reaction proceeds completely, is more troublesome. Many chemical reactions do not proceed to completion as written, for a variety of reasons. When we calculate an amount of product assuming that all the reactant reacts, we calculate the **theoretical yield**, an amount that is theoretically produced as calculated using the balanced chemical reaction.

In many cases, however, this is not what really happens. In many cases, less—sometimes, much less—of a product is made during the course of a chemical reaction. The amount that is actually produced in a reaction is called the **actual yield**. By definition, the actual yield is less than or equal to the theoretical yield. If it is not, then an error has been made.

Both theoretical yields and actual yields are expressed in units of moles or grams. It is also common to see something called a percent yield. The **percent yield** is a comparison between the actual yield and the theoretical yield and is defined as

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{6.5.1}$$

It does not matter whether the actual and theoretical yields are expressed in moles or grams, as long as they are expressed in the same units. However, the percent yield always has units of percent. Proper percent yields are between 0% and 100%. In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student must have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments. A 100% yield means that everything worked perfectly, and the chemist obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car's engine without spilling knows the unlikelihood of a 100% yield. At the other extreme, a yield of 0% means that no product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

Example 6.5.1:

A worker reacts 30.5 g of Zn with nitric acid and evaporates the remaining water to obtain 65.2 g of $Zn(NO_3)_2$. What are the theoretical yield, the actual yield, and the percent yield?

$$Zn\,(s) + 2\,HNO_3\,(aq) \longrightarrow Zn(NO_3)_2\,(aq) + H_2\,(g)$$

Solution

A mass-mass calculation can be performed to determine the theoretical yield. We need the molar masses of Zn (65.39 g/mol) and $Zn(NO_3)_2$ (189.41 g/mol). In three steps, the mass-mass calculation is:

$$30.5\ \cancel{g\ Zn} \times \frac{1\ \cancel{mol\ Zn}}{65.39\ \cancel{g\ Zn}} \times \frac{1\ \cancel{mol\ Zn(NO_3)_2}}{1\ \cancel{mol\ Zn}} \times \frac{189.41\ g\ Zn(NO_3)_2}{1\ \cancel{mol\ Zn(NO_3)_2}} = 88.3\ g\ Zn(NO_3)_2$$

Thus, the theoretical yield is 88.3 g of $Zn(NO_3)_2$. The actual yield is the amount that was actually made, which was 65.2 g of $Zn(NO_3)_2$. To calculate the percent yield, we take the actual yield and divide it by the theoretical yield and multiply by 100 (Equation 6.5.1):

$$\frac{65.2\ g\ Zn(NO_3)_2}{88.3\ g\ Zn(NO_3)_2} \times 100\% = 73.8\%$$

The worker achieved almost three-fourths of the possible yield.

? Exercise 6.5.1

A synthesis produced 2.05 g of NH_3 from 16.5 g of N_2. What is the theoretical yield and the percent yield?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

*Technically, this is a reversible reaction (with double arrows), but for this exercise consider it irreversible (single arrow).

Answer

theoretical yield = 20.1 g; percent yield = 10.2%

Chemistry is Everywhere: Actual Yields in Drug Synthesis and Purification

Many drugs are the product of several steps of chemical synthesis. Each step typically occurs with less than 100% yield, so the overall percent yield might be very small. The general rule is that the overall percent yield is the product of the percent yields of the individual synthesis steps. For a drug synthesis that has many steps, the overall percent yield can be very tiny, which is one factor in the huge cost of some drugs. For example, if a 10-step synthesis has a percent yield of 90% for each step, the overall yield for the entire synthesis is only 35%. Many scientists work every day trying to improve percent yields of the steps in the synthesis to decrease costs, improve profits, and minimize waste.

Even purifications of complex molecules into drug-quality purity are subject to percent yields. Consider the purification of impure albuterol. Albuterol ($C_{13}H_{21}NO_2$; accompanying figure) is an inhaled drug used to treat asthma, bronchitis, and other obstructive pulmonary diseases. It is synthesized from norepinephrine, a naturally occurring hormone and neurotransmitter. Its initial synthesis makes very impure albuterol that is purified in five chemical steps. The details of the steps do not concern us; only the percent yields do:

impure albuterol → intermediate A	percent yield = 70%
intermediate A → intermediate B	percent yield = 100%
intermediate B → intermediate C	percent yield = 40%
intermediate C → intermediate D	percent yield = 72%
intermediate D → purified albuterol	percent yield = 35%
overall percent yield = 70% × 100% × 40% × 72% × 35% = 7.5%	

That is, only about *one-fourteenth* of the original material was turned into the purified drug. This demonstrates one reason why some drugs are so expensive—a lot of material is lost in making a high-purity pharmaceutical.



Figure 6.5.1 A child using an albuterol inhaler, the container of albuterol medication, and a molecular model of the albuterol molecule. Source: Photo on far left © Thinkstock. Photo in center courtesy of Intropin, http://commons.wikimedia.org/wiki/Fi...te_%281%29.JPG.

Limiting Reagent

In all the examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants was left over at the end of the reaction. This is often desirable, as in the case of a space shuttle, where excess oxygen or hydrogen was not only extra freight to be hauled into orbit but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactant. The reactant that remains after a reaction has gone to completion is in excess.

Consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is thus

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{6.5.2}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

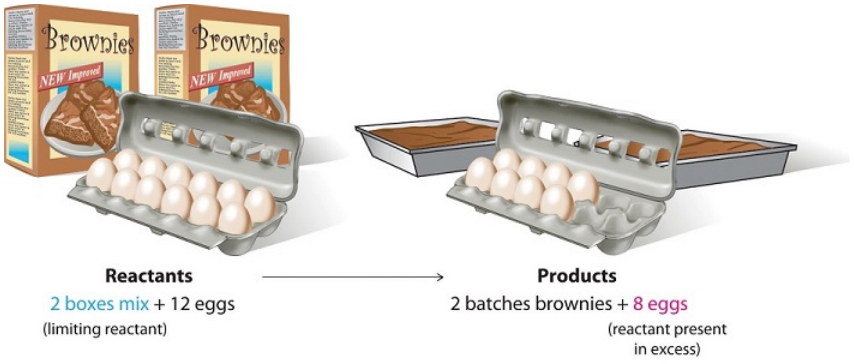


Figure 6.5.1: *The Concept of a Limiting Reactant in the Preparation of Brownies*

A similar situation exists for many chemical reactions: you usually run out of one reactant before all of the other reactant has reacted. The reactant you run out of is called the **limiting reagent**; the other reactant or reactants are considered to be *in excess*. A crucial skill in evaluating the conditions of a chemical process is to determine which reactant is the limiting reagent and which is in excess.

The key to recognizing which reactant is the limiting reagent is based on a mole-mass or mass-mass calculation: whichever reactant gives the *lesser* amount of product is the limiting reagent. What we need to do is determine an amount of one product (either moles or mass), assuming all of each reactant reacts. Whichever reactant gives the least amount of that particular product is the limiting reagent. It does not matter which product we use, as long as we use the same one each time. It does not matter whether we

determine the number of moles or grams of that product; however, we will see shortly that knowing the final mass of product can be useful.

For example, consider this reaction:

$$4As(s) + 3O_2(g) \rightarrow 2As_2O_3(s)$$

Suppose we start a reaction with 50.0 g of As and 50.0 g of O_2. Which one is the limiting reagent? We need to perform two mole-mass calculations, each assuming that each reactant reacts completely. Then we compare the amount of the product produced by each and determine which is less.

The calculations are as follows:

$$50.0\ \cancel{g\ As} \times \frac{1\ \cancel{mol\ As}}{74.92\ \cancel{g\ As}} \times \frac{2\ mol\ As_2O_3}{4\ \cancel{mol\ As}} = 0.334\ mol\ As_2O_3$$

$$50.0\ \cancel{g\ O_2} \times \frac{1\ \cancel{mol\ O_2}}{32.00\ \cancel{g\ O_2}} \times \frac{2\ mol\ As_2O_3}{3\ \cancel{mol\ O_2}} = 1.04\ mol\ As_2O_3$$

Comparing these two answers, it is clear that 0.334 mol of As_2O_3 is less than 1.04 mol of As_2O_3, so arsenic is the limiting reagent. If this reaction is performed under these initial conditions, the arsenic will run out before the oxygen runs out. We say that the oxygen is "in excess."

Identifying the limiting reagent, then, is straightforward. However, there are usually two associated questions: (1) what mass of product (or products) is then actually formed? and (2) what mass of what reactant is left over? The first question is straightforward to answer: simply perform a conversion from the number of moles of product formed to its mass, using its molar mass. For As_2O_3, the molar mass is 197.84 g/mol; knowing that we will form 0.334 mol of As_2O_3 under the given conditions, we will get

$$0.334\ \cancel{mol\ As_2O_3} \times \frac{197.84\ g\ As_2}{1\ \cancel{mol\ As_2O_3}} = 66.1\ g\ As_2O_3$$

The second question is somewhat more convoluted to answer. First, we must do a mass-mass calculation relating the limiting reagent (here, As) to the other reagent (O_2). Once we determine the mass of O_2 that reacted, we subtract that from the original amount to determine the amount left over. According to the mass-mass calculation,

$$50.0\ \cancel{g\ As} \times \frac{1\ \cancel{mol\ As}}{74.92\ \cancel{g\ As}} \times \frac{3\ \cancel{mol\ O_2}}{4\ \cancel{mol\ As}} \times \frac{32.00\ g\ O_2}{1\ \cancel{mol\ O_2}} = 16.0\ g\ O_2\ reacted$$

Because we reacted 16.0 g of our original O_2, we subtract that from the original amount, 50.0 g, to get the mass of O_2 remaining:

50.0 g O_2 − 16.0 g O_2 reacted = 34.0 g O_2 left over

You must remember to perform this final subtraction to determine the amount remaining; a common error is to report the 16.0 g as the amount remaining.

Example 6.5.1:

A 5.00 g quantity of Rb is combined with 3.44 g of $MgCl_2$ according to this chemical reaction:

$$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$

What mass of Mg is formed, and what mass of what reactant is left over?

Solution

Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations and determine which amount is less.

$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ Mg}}{2\ \cancel{mol\ Rb}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.711\ g\ Mg$$

$$3.44\ g\ \cancel{MgCl_2} \times \frac{1\ \cancel{mol\ MgCl_2}}{95.21\ g\ \cancel{MgCl_2}} \times \frac{1\ \cancel{mol\ Mg}}{1\ \cancel{mol\ MgCl_2}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.878\ g\ Mg$$

The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reagent. To determine how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass of MgCl2 reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount.

$$5.00\ g\ \cancel{Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ g\ \cancel{Rb}} \times \frac{1\ \cancel{mol\ MgCl_2}}{2\ \cancel{mol\ Rb}} \times \frac{95.21\ g\ Mg}{1\ \cancel{mol\ MgCl_2}} = 2.78\ g\ MgCl_2\ \ reacted$$

Because we started with 3.44 g of MgCl2, we have

3.44 g MgCl2 − 2.78 g MgCl2 reacted = 0.66 g MgCl2 left

Exercise 6.5.1

Given the initial amounts listed, what is the limiting reagent, and what is the mass of the leftover reagent?

$$\underbrace{22.7\ g}_{MgO(s)} + \underbrace{17.9\ g}_{H_2S} \rightarrow MgS(s) + H_2O(l)$$

Answer

H_2S is the limiting reagent; 1.5 g of MgO are left over.

Summary

Theoretical yield is the calculated yield using the balanced chemical reaction. Actual yield is what is actually obtained in a chemical reaction. Percent yield is a comparison of the actual yield with the theoretical yield.

The limiting reagent is the reactant that produces the least amount of product. Mass-mass calculations can determine how much product is produced and how much of the other reactants remain.

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6.E: Quantities in Chemical Reactions (Exercise)

6.1: The Mole

Concept Review Exercise

1. What is a mole?

Answer

1. A mole is 6.022×10^{23} things.

Exercises

1. How many dozens are in 1 mol? Express your answer in proper scientific notation.
2. A gross is a dozen dozen, or 144 things. How many gross are in 1 mol? Express your answer in proper scientific notation.
3. How many moles of each type of atom are in 1.0 mol of $C_6H_{12}O_6$?
4. How many moles of each type of atom are in 1.0 mol of $K_2Cr_2O_7$?
5. How many moles of each type of atom are in 2.58 mol of Na_2SO_4?
6. How many moles of each type of atom are in 0.683 mol of $C_{34}H_{32}FeN_4O_4$? (This is the formula of heme, a component of hemoglobin.)
7. How many molecules are in 16.8 mol of H_2O?
8. How many formula units are in 0.778 mol of iron(III) nitrate?
9. A sample of gold contains 7.02×10^{24} atoms. How many moles of gold is this?
10. A flask of mercury contains 3.77×10^{22} atoms. How many moles of mercury are in the flask?
11. An intravenous solution of normal saline may contain 1.72 mol of sodium chloride (NaCl). How many sodium and chlorine atoms are present in the solution?
12. A lethal dose of arsenic is 1.00×10^{21} atoms. How many moles of arsenic is this?

Answers

1. 5.018×10^{22} dozens

2. 4.18 x 10^{21} grosses

3. 6.0 mol of C atoms, 12.0 mol of H atoms, and 6.0 mol of O atoms

4. 2.0 mol of K atoms, 2.0 mol of Cr atoms, and 7.0 mol of O atoms

5. 5.16 mol of Na atoms, 2.58 mol of S atoms, and 10.32 mol of O atoms

6. 23.2 mol of C atoms, 21.9 mol of H atoms, 0.683 mol of Fe, 2.73 mol of N and 2.73 mol of O atoms

7. 1.012×10^{25} molecules

8. 4.69 x 10^{23} formula units

9. 11.7 mol

10. 0.0626 mol

11. 1.04×10^{24} Na atoms and 1.04×10^{24} Cl atoms

12. 0.00166 mol

6.2: Atomic and Molar Masses

Concept Review Exercises

1. How are molar masses of the elements determined?
2. How are molar masses of compounds determined?

Answers

1. Molar masses of the elements are the same numeric value as the masses of a single atom in atomic mass units but in units of grams instead.
2. Molar masses of compounds are calculated by adding the molar masses of their atoms.

Exercises

1. What is the molar mass of Si? What is the molar mass of U?
2. What is the molar mass of Mn? What is the molar mass of Mg?
3. What is the molar mass of $FeCl_2$? What is the molar mass of $FeCl_3$?
4. What is the molar mass of C_6H_6? What is the molar mass of $C_6H_5CH_3$?
5. What is the molar mass of $(NH_4)_2S$? What is the molar mass of $Ca(OH)_2$?
6. What is the molar mass of $(NH_4)_3PO_4$? What is the molar mass of $Sr(HCO_3)_2$?
7. Aspirin ($C_9H_8O_4$) is an analgesic (painkiller) and antipyretic (fever reducer). What is the molar mass of aspirin?
8. Ibuprofen ($C_{13}H_{18}O_2$) is an analgesic (painkiller). What is the molar mass of ibuprofen?
9. Morphine ($C_{17}H_{19}NO_3$) is a narcotic painkiller. What is the mass of 1 mol of morphine?
10. Heroin ($C_{21}H_{23}NO_5$) is a narcotic drug that is a derivative of morphine. What is the mass of 1 mol of heroin?

Answers

1. 28.09 g/mol; 238.0 g/mol
2. 54.94 g/mol; 24.31 g/mol
3. 126.75 g/mol; 162.20 g/mol
4. 78.12 g/mol; 92.15 g/mol
5. 68.16 g/mol; 74.10 g/mol
6. 149.12 g/mol; 209.64 g/mol
7. 180.17 g/mol
8. 206.31 g/mol
9. 285.37 g
10. 369.45 g

6.3: Mole-Mass Conversions

Concept Review Exercises

1. What relationship is needed to perform mole-mass conversions?
2. What information determines which conversion factor is used in a mole-mass conversion?

Answers

1. The atomic or molar mass is needed for a mole-mass conversion.
2. The unit of the initial quantity determines which conversion factor is used.

Exercises

1. What is the mass of 8.603 mol of Fe metal?
2. What is the mass of 0.552 mol of Ag metal?
3. What is the mass of 6.24×10^4 mol of Cl_2 gas?
4. What is the mass of 0.661 mol of O_2 gas?
5. What is the mass of 20.77 mol of $CaCO_3$?
6. What is the mass of 9.02×10^{-3} mol of the hormone epinephrine ($C_9H_{13}NO_3$)?
7. How many moles are present in 977.4 g of $NaHCO_3$?

8. How many moles of erythromycin ($C_{37}H_{67}NO_{13}$), a widely used antibiotic, are in 1.00×10^3 g of the substance?
9. Cortisone ($C_{21}H_{28}O_5$) is a synthetic steroid that is used as an anti-inflammatory drug. How many moles of cortisone are present in one 10.0 mg tablet?
10. Recent research suggests that the daily ingestion of 85 mg of aspirin (also known as acetylsalicylic acid, $C_9H_8O_4$) will reduce a person's risk of heart disease. How many moles of aspirin is that?

Answers

1. 480.5 g
2. 59.6 g
3. 4.42×10^6 g
4. 21.2 g
5. 2,079 g
6. 1.65 g
7. 11.63 mol
8. 1.36 mol
9. 2.77×10^{-5} mol
10. 4.7×10^{-4} mol

6.4: Mole-Mole Relationships in Chemical Reactions

Concept Review Exercise

1. How do we relate molar amounts of substances in chemical reactions?

Answer

1. Amounts of substances in chemical reactions are related by their coefficients in the balanced chemical equation.

Exercises

1. List the molar ratios you can derive from this balanced chemical equation:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

2. List the molar ratios you can derive from this balanced chemical equation

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

3. Given the following balanced chemical equation,

$$6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O$$

how many moles of NaCl can be formed if 3.77 mol of NaOH were to react?

4. Given the following balanced chemical equation,

$$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$$

how many moles of H_2O can be formed if 0.0652 mol of C_5H_{12} were to react?

5. Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react.

$$NH_3 + O_2 \rightarrow N_2 + H_2O$$

6. Trinitrotoluene [$C_6H_2(NO_2)_3CH_3$], also known as TNT, is formed by reacting nitric acid (HNO_3) with toluene ($C_6H_5CH_3$):

$$HNO_3 + C_6H_5CH_3 \rightarrow C_6H_2(NO_2)_3CH_3 + H_2O$$

Balance the equation and determine how many moles of TNT are produced when 4.903 mol of HNO_3 react.

7. Chemical reactions are balanced in terms of molecules and in terms of moles. Are they balanced in terms of dozens? Defend your answer.
8. Explain how a chemical reaction balanced in terms of moles satisfies the law of conservation of matter.

Answers

1. 1 mol NH_3:2 mol O_2:1 mol HNO_3:1 mol H_2O

2. 2 mol C_2H_2:5 mol O_2:4 mol CO_2:2 mol H_2O

3. 3.14 mol

4. 0.3912 mol

5. $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol

6. $3HNO_3 + C_6H_5CH_3 \rightarrow C_6H_2(NO_2)_3CH_3 + 3H_2O$; 1.634 mol

7. Yes, they are still balanced.

8. A chemical reaction, balanced in terms of moles, contains the same number of atoms of each element, before and after the reaction. This means that all the atoms and its masses are conserved.

6.5: Mole-Mass and Mass-Mass Problems

Concept Review Exercises

1. What is the general sequence of conversions for a mole-mass calculation?
2. What is the general sequence of conversions for a mass-mass calculation?

Answers

1. mol first substance → mol second substance → mass second substance
2. mass first substance → mol first substance → mol second substance → mass second substance

Exercises

1. Given the following unbalanced chemical equation,

$$H_3PO_4 + NaOH \rightarrow H_2O + Na_3PO_4$$

what mass of H_2O is produced by the reaction of 2.35 mol of H_3PO_4?

2. Given the following unbalanced chemical equation,

$$C_2H_6 + Br_2 \rightarrow C_2H_4Br_2 + HBr$$

what mass of HBr is produced if 0.884 mol of C_2H_6 is reacted?

3. Certain fats are used to make soap, the first step being to react the fat with water to make glycerol (also known as glycerin) and compounds called fatty acids. One example is as follows:

$$\underset{\text{a fat}}{C_3H_5(OOC(CH_2)_{14}CH_3)_3} + 3H_2O \rightarrow \underset{\text{glycerol}}{C_3H_5(OH)_3} + 3\underset{\text{fatty acid}}{CH_3(CH_2)_{14}COOH}$$

How many moles of glycerol can be made from the reaction of 1,000.0 g of $C_3H_5(OOC(CH_2)_{14}CH_3)_3$?

4. Photosynthesis in plants leads to the general overall reaction for producing glucose ($C_6H_{12}O_6$):

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

How many moles of glucose can be made from the reaction of 544 g of CO_2?

5. Precipitation reactions, in which a solid (called a precipitate) is a product, are commonly used to remove certain ions from solution. One such reaction is as follows:

$$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

How many grams of Na_2SO_4 are needed to precipitate all the barium ions produced by 43.9 g of $Ba(NO_3)_2$?

6. Nitroglycerin [$C_3H_5(ONO_2)_3$] is made by reacting nitric acid (HNO_3) with glycerol [$C_3H_5(OH)_3$] according to this reaction:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(ONO_2)_3 + 3H_2O$$

If 87.4 g of HNO_3 are reacted with excess glycerol, what mass of nitroglycerin can be made?

7. Antacids are bases that neutralize acids in the digestive tract. Magnesium hydroxide [$Mg(OH)_2$] is one such antacid. It reacts with hydrochloric acid in the stomach according to the following reaction:

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

How many grams of HCl can a 200 mg dose of $Mg(OH)_2$ neutralize?

8. Acid rain is caused by the reaction of nonmetal oxides with water in the atmosphere. One such reaction involves nitrogen dioxide (NO_2) and produces nitric acid (HNO_3):

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

If 1.82×10^{13} g of NO_2 enter the atmosphere every year due to human activities, potentially how many grams of HNO_3 can be produced annually?

9. A simplified version of the processing of iron ore into iron metal is as follows:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

How many grams of C are needed to produce 1.00×10^9 g of Fe?

10. The *SS Hindenburg* contained about 5.33×10^5 g of H_2 gas when it burned at Lakehurst, New Jersey, in 1937. The chemical reaction is as follows:

$$2H_2 + O_2 \rightarrow 2H_2O$$

How many grams of H_2O were produced?

Answers

1. 127 g
2. 143 g
3. 1.238 mol
4. 2.06 mol
5. 23.9 g
6. 105 g
7. 0.250 g
8. 1.66×10^{13} g
9. 1.61×10^8 g
10. 4.75×10^6 g

Additional Exercises

1. If the average male has a body mass of 70 kg, of which 60% is water, how many moles of water are in an average male?
2. If the average female is 60.0 kg and contains 0.00174% iron, how many moles of iron are in an average female?
3. How many moles of each element are present in 2.67 mol of each compound?
   a. HCl
   b. H_2SO_4
   c. $Al(NO_3)_3$
   d. $Ga_2(SO_4)_3$

4. How many moles of each element are present in 0.00445 mol of each compound?
    a. HCl
    b. H_2SO_4
    c. $Al_2(CO_3)_3$
    d. $Ga_2(SO_4)_3$
5. What is the mass of one hydrogen atom in grams? What is the mass of one oxygen atom in grams? Do these masses have a 1:16 ratio, as expected?
6. What is the mass of one sodium atom in grams?
7. If 6.63×10^{-6} mol of a compound has a mass of 2.151 mg, what is the molar mass of the compound?
8. Hemoglobin (molar mass is approximately 64,000 g/mol) is the major component of red blood cells that transports oxygen and carbon dioxide in the body. How many moles are in 0.034 g of hemoglobin?

Answers

1. 2,330 mol

2. 0.0187 mol

3. a. 2.67 mol of H and 2.67 mol of Cl
    b. 5.34 mol of H, 2.67 mol of S, and 10.68 mol of O
    c. 2.67 mol of Al, 8.01 mol of N, and 24.03 mol of O
    d. 5.34 mol of Ga, 8.01 mol of S, and 32.04 mol of O

4.
    a. 0.00445 mol of H and 0.00445 mol of Cl
    b. 0.00890 mol of H, 0.00445 mol of S, and 0.0178 mol of O
    c. 0.00890 mol of Al, 0.0134 mol of C, and 0.0401 mol of O
    d. 0.00890 mol of Ga, 0.0134 mol of S, and 0.0534 mol of O

5. H = 1.68×10^{-24} g and O = 2.66×10^{-23} g; yes, they are in a 1:16 ratio.

6. 3.819×10^{-23} g

7. 324 g/mol

8. 5.3×10^{-7} mol

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6.S: Quantities in 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.

Chemical reactions relate quantities of reactants and products. Chemists use the **mole** unit to represent 6.022×10^{23} things, whether the things are atoms of elements or molecules of compounds. This number, called **Avogadro's number**, is important because this number of atoms or molecules has the same mass in grams as one atom or molecule has in atomic mass units. **Molar masses** of substances can be determined by summing the appropriate masses from the periodic table; the final molar mass will have units of grams.

Because one mole of a substance will have a certain mass, we can use that relationship to construct conversion factors that will convert a mole amount into a mass amount, or vice versa. Such **mole-mass conversions** typically take one algebraic step.

Chemical reactions list reactants and products in molar amounts, not just molecular amounts. We can use the coefficients of a balanced chemical equation to relate moles of one substance in the reaction to moles of other substances (stoichiometry). Chemical reactions obey the Law of Conservation of Mass. To balance a chemical reaction, the coefficients in front of each compound can be adjusted until the total number of atoms of each elements is equal on both sides of the reaction arrow.

Collision Theory can be used to described the energetic aspects of chemical reactions. The reactants and products of a chemical reaction store potential energy in the form of chemical bonds and intermolecular forces. The energy difference in the bond energies of the reactants and products is called "Enthalpy". When the products are lower in potential energy than the reactants, then this excess energy is released as heat and the reaction is described as exothermic. When the products are higher in potential energy than the reactants, then energy must be added to the reaction as heat for it to occur and the reaction is described as endothermic.

The rate of a chemical reaction is influenced by its activation energy. The larger the activation energy, the slower the reaction rate. Catalysts can be added to reactions to lower the activation energy and increase the reaction rate.

Not all reactions go to completion. For some reactions, both the forward and reverse reaction can occur simultaneously. When the forward and reverse reaction rates are equal, the reaction is described as being "at equilibrium". Another way to recognize when a system is at equilibrium is when the concentration of reactants and products remain constant. Le Chatlier's principle states that the direction of an equilibrium reaction will shift to reduce the stress.

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CHAPTER OVERVIEW

7: 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.

7.0: Prelude to Energy and Chemical Processes
7.1: Energy and Its Units
7.2: Heat and Temperature
7.3: Phase Changes
7.4: Bond Energies and Chemical Reactions
7.5: The Energy of Biochemical Reactions
7.6: Reversible Reactions and Chemical Equilibrium
7.7: Equilibrium Equations and Equilibrium Constants
7.8: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
7.E: Energy and Chemical Processes (Exercises)
7.S: Energy and Chemical Processes (Summary)

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7.0: 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 7.0.1: 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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7.1: 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:

$$1\ cal = 4.184\ J$$

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 7.1.1

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.

7.1.1 Exercise

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 7.1.1 shows an example.

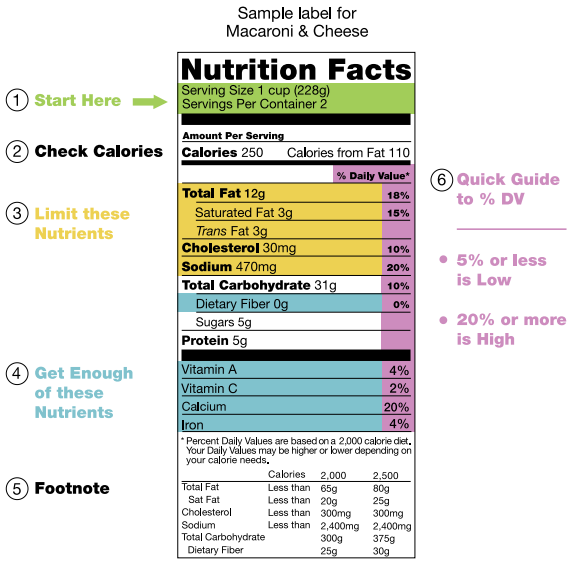


Figure 7.1.1: Figure 7.1.1: Nutritional Energy. A sample nutrition facts label, with instructions from the U.S. Food and Drug Administration. from Wikipedia.

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 7.1.1 for a slice of roast beef.

Table 7.1.1: 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 7.1.2.

Table 7.1.2: 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 7.1.3 lists the energy expenditure for a variety of exercises.

Table 7.1.3: 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.

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7.2: Heat and Temperature

Learning Objectives

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

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

Temperature Scales

Temperature is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees. There are three scales used for reporting temperatures. Figure 7.2.1 compares the three temperature scales: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

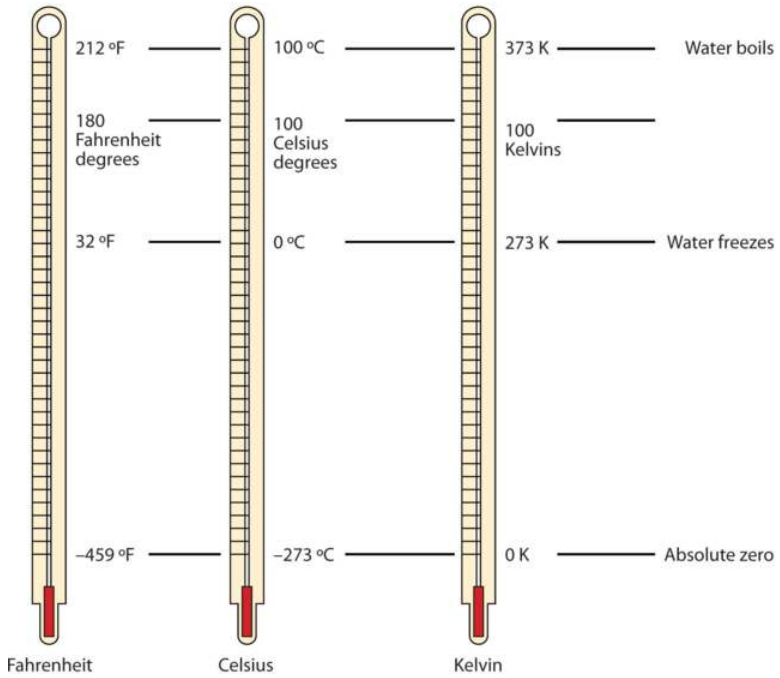


Figure 7.2.1: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales. These thermometers have a red-colored liquid which contains alcohol and food coloring. Silver looking thermometers contain mercury, which is a neurotoxin.

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

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

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

$$^{\circ}C = (^{\circ}F - 32) \times \frac{5}{9} \tag{7.2.1}$$

$$^{\circ}F = \left(^{\circ}C \times \frac{9}{5}\right) + 32 \tag{7.2.2}$$

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

Example 7.2.1: Conversions

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

Solution

a. Using Equation 7.2.1, we have

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

b. Using Equation 7.2.2, we have

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

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

Exercise 7.2.1

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

Answer a

−17.8°C

Answer b

414°F

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

$$K =^{\circ} C + 273.15 \tag{7.2.3}$$

For most purposes, it is acceptable to use 273 instead of 273.15 in Equation 7.2.3.

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

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

Example 7.2.2: Room Temperature

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

Solution

First, we use Equation 7.2.1 to determine the temperature in degrees Celsius:

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

Then we use Equation 7.2.3 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. The relationship between the amount of heat transferred and the temperature change can be written as

$$\text{heat} \propto \Delta T \tag{7.2.4}$$

where ∝ means “is proportional to” and **Δ*T* is the change in temperature of the system**. Any change in a variable is always defined as “the final value minus the initial value” of the variable, so Δ*T* is $T_{\text{final}} - T_{\text{initial}}$. In addition, the greater the mass of an object, the more heat is needed to change its temperature. We can include a variable representing mass (*m*) to the proportionality as follows:

$$\text{heat} \propto m\Delta T \tag{7.2.5}$$

To change this proportionality into an equality, we include a proportionality constant. The proportionality constant is called the specific heat and is commonly symbolized by c:

$$\text{heat} = mc\Delta T \tag{7.2.6}$$

Every substance has a characteristic **specific heat**, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express Δ*T*. The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°C. Table 7.2.1 lists the specific heats for various materials.

Table 7.2.1: Specific Heats of Selected Substances

Substance	c (cal/g•°C)
aluminum (Al)	0.215
aluminum oxide (Al_2O_3)	0.305
benzene (C_6H_6)	0.251
copper (Cu)	0.092
ethanol (C_2H_6O)	0.578
hexane (C_6H_{14})	0.394
hydrogen (H_2)	3.419
ice [$H_2O(s)$]	0.492
iron (Fe)	0.108
iron(III) oxide (Fe_2O_3)	0.156
mercury (Hg)	0.033
oxygen (O_2)	0.219
sodium chloride (NaCl)	0.207
steam [$H_2O(g)$]	0.488
water [$H_2O(\ell)$]	1.00

> *The proportionality constant c is sometimes referred to as the specific heat capacity or (incorrectly) the heat capacity.*

The *direction* of heat flow is not shown in heat = $mc\Delta T$. If energy goes into an object, the total energy of the object increases, and the values of heat ΔT are positive. If energy is coming out of an object, the total energy of the object decreases, and the values of heat and ΔT are negative.

Example 7.2.3

What quantity of heat is transferred when a 150.0 g block of iron metal is heated from 25.0°C to 73.3°C? What is the direction of heat flow?

Solution

We can use Equation 7.2.6 to determine the amount of heat, but first we need to determine ΔT. Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, ΔT is as follows:

$$\begin{aligned}\Delta T &= T_{final} - T_{initial} \\ &= 73.3^oC - 25.0^oC \\ &= 48.3^oC\end{aligned}$$

The mass is given as 150.0 g, and Table 7.2.1 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into Equation 7.2.6 and solve for amount of heat:

$$\text{heat} = (150.0\text{ g})\left(0.108\ \frac{\text{cal}}{\text{g}\cdot{}^\circ\text{C}}\right)(48.3^\circ\text{C}) = 782\text{ cal}$$

Note how the gram and °C units cancel algebraically, leaving only the calorie unit, which is a unit of heat. Because the temperature of the iron increases, energy (as heat) must be flowing *into* the metal.

7.2.3 Exercise

What quantity of heat is transferred when a 295.5 g block of aluminum metal is cooled from 128.0°C to 22.5°C? What is the direction of heat flow?

Answer

6,700 cal

Example 7.2.4

A 10.3 g sample of a reddish-brown metal gave off 71.7 cal of heat as its temperature decreased from 97.5°C to 22.0°C. What is the specific heat of the metal? Can you identify the metal from the data in Table 7.2.1?

Solution

The question gives us the heat, the final and initial temperatures, and the mass of the sample. The value of ΔT is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0^\circ\text{C} - 97.5^\circ\text{C} = -75.5^\circ\text{C}$$

If the sample gives off 71.7 cal, it loses energy (as heat), so the value of heat is written as a negative number, −71.7 cal. Substitute the known values into heat = $mc\Delta T$ and solve for c:

$$-71.7\text{ cal} = (10.3\text{ g})(c)(-75.5^\circ\text{C})$$

$$c = \frac{-71.7\text{ cal}}{(10.3\text{ g})(-75.5^\circ\text{C})}$$

$$c = 0.0923\text{ cal/g}\bullet{}^\circ\text{C}$$

This value for specific heat is very close to that given for copper in Table 7.2.1.

7.2.4 Exercise

A 10.7 g crystal of sodium chloride (NaCl) had an initial temperature of 37.0°C. What is the final temperature of the crystal if 147 cal of heat were supplied to it?

Answer

103.4°C

Notice that water has a very high specific heat compared to most other substances. Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see table above). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.



Figure 7.2.2: This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.

Summary

- Heat transfer is related to temperature change.
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}C$.

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7.3: 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.

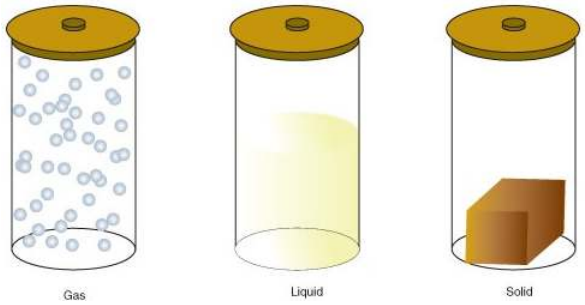


Figure 7.3.1: States of Matter. All three containers contain a substance with the same mass, but the substances are in different states. In the left-hand container, the substance is a gas, which has spread to fill its container. It takes both the shape and volume of the container. In the middle container, 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:

Changes of State

Phase to Phase transition	Transition Name
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 7.3.1

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.

Solution 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.

7.3.1 Exercise

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 7.3.1).

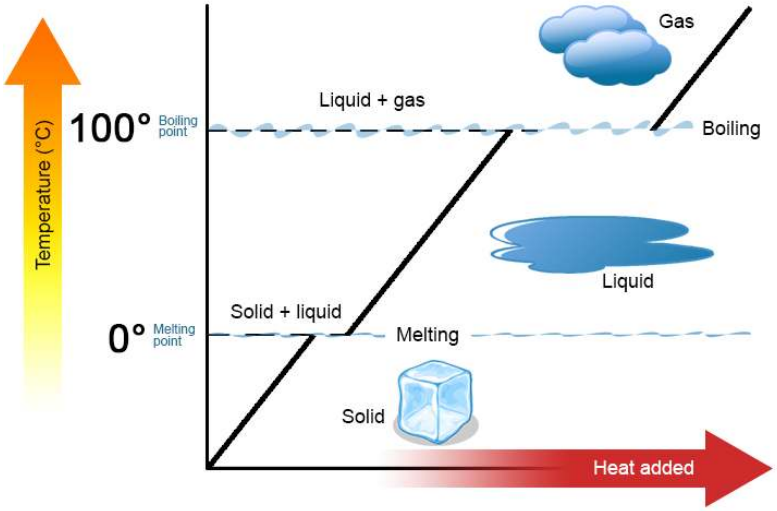


Figure 7.3.2: Heating curve for water. As heat is added to solid water, the temperature increases until it reaches 0 °C, the melting point. At this point, the phase change, added heat goes into changing the state from a solid to liquid. Only when this phase change is complete, the temperature can increase. (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 7.3.1, **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.

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion (ΔH_{fus}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. The heat of vaporization (ΔH_{vap}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the boiling point. If you know the total number of grams or moles of material, you can use the ΔH_{fus} or the ΔH_{vap} to determine the total heat being transferred for melting or solidification using these expressions:

$$\text{heat} = n \times \Delta H_{fus}$$

where n is the number of moles and ΔH_{fus} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{fus}$$

where m is the mass in grams and ΔH_{fus} is expressed in energy/gram.

For the boiling or condensation, use these expressions:

$$\text{heat} = n \times \Delta H_{vap}$$

where n is the number of moles) and ΔH_{vap} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{vap}$$

where m is the mass in grams and ΔH_{vap} is expressed in energy/gram.

Remember that a phase change depends on the direction of the heat transfer. If heat transfers in, solids become liquids, and liquids become solids at the melting and boiling points, respectively. If heat transfers out, liquids solidify, and gases condense into liquids. At these points, there are no changes in temperature as reflected in the above equations.

Example 7.3.2

How much heat is necessary to melt 55.8 g of ice (solid H_2O) at 0°C? The heat of fusion of H_2O is 79.9 cal/g.

Solution

We can use the relationship between heat and the heat of fusion (Equation 7.3.1) to determine how many cal of heat are needed to melt this ice:

$$\text{heat} = \text{m} \times \Delta\text{H}_{\text{fus}}$$

$$\text{heat} = (55.8 \cancel{\text{g}}) \left(\frac{79.9 \text{ cal}}{\cancel{\text{g}}} \right) = 4,460 \text{ cal}$$

Exercise 7.3.2

How much heat is necessary to vaporize 685 g of H_2O at 100°C? The heat of vaporization of H_2O is 540 cal/g.

Answer

$$\text{heat} = \text{m} \times \Delta\text{H}_{\text{vap}}$$

$$\text{heat} = (685 \cancel{\text{g}}) \left(\frac{540 \text{ cal}}{\cancel{\text{g}}} \right) = 370,000 \text{ cal}$$

Table 7.3.1 lists the heats of fusion and vaporization for some common substances. Note the units on these quantities; when you use these values in problem solving, make sure that the other variables in your calculation are expressed in units consistent with the units in the specific heats or the heats of fusion and vaporization.

Table 7.3.1: Heats of Fusion and Vaporization for Selected Substances

Substance	ΔH_{fus} (cal/g)	ΔH_{vap} (cal/g)
aluminum (Al)	94.0	2,602
gold (Au)	15.3	409
iron (Fe)	63.2	1,504
water (H_2O)	79.9	540
sodium chloride (NaCl)	123.5	691
ethanol (C_2H_5OH)	45.2	200.3
benzene (C_6H_6)	30.4	94.1

Sublimation

There is also a phase change where a solid goes directly to a gas:

\[\text{solid} \rightarrow \text{gas} \nonumber\]

This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO_2). At −78.5°C (−109°F), solid carbon dioxide sublimes, changing directly from the solid phase to the gas phase:

$$\text{CO}_2(\text{s}) \xrightarrow{-78.5^\circ\text{C}} \text{CO}_2(\text{g})$$

Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it does directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C, solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimes, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimes, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a "burn," and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer's temperature and by wrapping foods tightly so water does not have any space to sublime into.

Key Takeaway

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

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7.4: Bond Energies and Chemical Reactions

Learning Objectives

The Learning Objectives of this Module are to:

- Define *bond energy*.
- Calculate enthalpy change or heat of reaction.
- Determine if a chemical process is exothermic or endothermic.

What happens when you take a basketball, place it halfway up a playground slide, and then let it go? The basketball rolls down the slide. What happens if you do it again? Does the basketball roll down the slide? It should.

If you were to perform this experiment over and over again, do you think the basketball would ever roll *up* the slide? Probably not. Why not? Well, for starters, in all of our experience, the basketball has always moved to a lower position when given the opportunity. The gravitational attraction of Earth exerts a force on the basketball, and given the chance, the basketball will move down. We say that the basketball is going to a lower *gravitational potential energy*. The basketball can move up the slide, but only if someone exerts some effort (that is, work) on the basketball. A general statement, based on countless observations over centuries of study, is that all objects tend to move spontaneously to a position of minimum energy unless acted on by some other force or object.

Bond Energy

A similar statement can be made about atoms in compounds. Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.* In making compounds, atoms act like a basketball on a playground slide; they move in the direction of decreasing energy.

We can reverse the process, just as with the basketball. If we put energy into a molecule, we can cause its bonds to break, separating a molecule into individual atoms. Bonds between certain specific elements usually have a characteristic energy, called the bond energy, that is needed to break the bond. The same amount of energy was liberated when the atoms made the chemical bond in the first place. The term *bond energy* is usually used to describe the strength of interactions between atoms that make covalent bonds. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. The C=C bond is stronger than C-C (as discussed in relation to bond length in Section 4.4). For atoms in ionic compounds attracted by opposite charges, the term lattice energy is used. For now, we will deal with covalent bonds in molecules.

Although each molecule has its own characteristic bond energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. Table 7.4.1 lists the approximate bond energies of various covalent bonds.

Table 7.4.1: Approximate Bond Energies

Bond	Bond Energy (kcal/mol)
C–H	100
C–O	86
C=O	190
C–N	70
C–C	85
C=C	145
C≡C	200
N–H	93
H–H	105
Br-Br	46
Cl–Cl	58
O–H	110
O=O	119
H–Br	87
H–Cl	103

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*. The enthalpy change, for a given reaction can be calculated using the bond energy values from Table 7.4.1.

Enthalpy Change or Heat of Reaction, Δ*H*

Energy changes in chemical reactions are usually measured as changes in enthalpy. In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

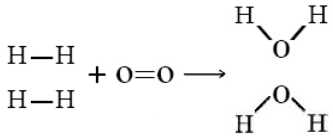
$$\text{enthalpy change} \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

The ≈ sign is used because we are adding together *average* bond energies (i.e., over many different molecules). Hence, this approach does not give exact values for the enthalpy change, Δ*H*.

Let's consider the reaction of 2 mols of hydrogen gas (H_2) with 1 mol of oxygen gas (O_2) to give 2 mol water:

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$$

or shown graphically:



with these average bond energies involved:

- H–H = 105 kcal/mol
- O=O = 119 kcal/mol

- O–H = 110 kcal/mol

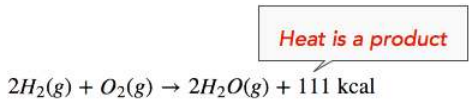
In this reaction, 2 H–H bonds and 1 O=O bonds are broken, while 4 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated and calculated as follows:

2 H–H bonds and 1 O=O bonds are broken, while 4 O–H bonds (two for each H2O) are formed. The energy changes can be tabulated and calculated as follows:

Bonds Broken (kcal/mol)		Bonds Formed (kcal/mol)	
2 H–H	2 mol x 105 kcal/mol = 210 kcal	4 O–H	4 mols x 110 kcal/mol = 440 kcal
1 O=O	1 mol x 119 kcal/mol = 119 kcal		
	Total = 329 kcal		**Total** = 440 kcal

$$\begin{aligned}\Delta H &\approx \sum(\text{bonds broken}) - \sum(\text{bonds formed}) \\ &\approx 329 \text{ kcal} - 440 \text{ kcal} \\ &\approx -111 \text{ kcal}\end{aligned}$$

The enthalpy change (ΔH) of the reaction is approximately −111 kcal/mol. This means that bonds in the products (440 kcal) are stronger than the bonds in the reactants (329 kcal) by about 111 kcal/mol. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes. This excess energy is **released** as heat, so the reaction is **exothermic**. Hence, we can re-write the reaction with the heat released (111 kcal) on the **product side** of the equation, as follows:



We can also re-write the reaction equation with the ΔH information (see below). Note that an **exothermic** reaction has a **negative ΔH** value.

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \qquad \Delta H = -111 \text{ kcal}$$

Example 7.4.1

What is the enthalpy change for this reaction? Is the reaction exothermic or endothermic?

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

Solution

Step 1- First look at the equation and identify which bonds exist on in the reactants (bonds broken).

- one H-H bond and
- one Br-Br bond

Step 2- Do the same for the products (bonds formed)

- two H-Br bonds

Step 3- Identify the bond energies of these bonds from Table 7.4.1:

- H-H bonds: 105 kcal/mol
- Br-Br bonds: 46 kcal/mol

Step 4- Set up the table (see below) and apply the formula for enthalpy change.

Solutions to Example 7.4.1

Bonds Broken (kcal/mol)		Bonds Formed (kcal/mol)	
1 H–H	1 mol x 105 kcal/mol = 105 kcal	2 H–*Br*	2 mols x 87 kcal/mol = 174 kcal
1 Br–Br	1 mol x 46 kcal/mol = 46 kcal		
	Total = 151 kcal		**Total** = 174 kcal

$$\Delta H \approx 151 \text{ kcal} - 174 \text{ kcal}$$
$$\approx -23 \text{ kcal}$$

Step 5- Since ΔH is negative (−23 kcal), the reaction is *exothermic*.

7.4.1Exercise

Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$\mathrm{H_2\,(g) + Cl_2\,(g)\ \rightarrow 2\,HCl\,(g)}$$

Is the reaction written above exothermic or endothermic? Explain.

Answer

ΔH = −43 kcal

Since ΔH is negative (−43 kcal), the reaction is *exothermic*.

Endothermic and Exothermic Reactions

Endothermic and exothermic reactions can be thought of as having energy as either a reactant of the reaction or a product. **Endothermic** reactions require energy, so energy is a reactant. Heat flows from the surroundings to the system (reaction mixture) and the enthalpy of the system increases (ΔH is positive). As discussed in the previous section, in an **exothermic** reaction, heat is released (considered a product) and the enthalpy of the system decreases (ΔH is negative).

In the course of an **endothermic** process, the system gains heat from the surroundings and so the **temperature of the surroundings decreases (gets cold).** A chemical reaction is **exothermic** if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, **the temperature of the surroundings increases.** See Figure 7.4.1.

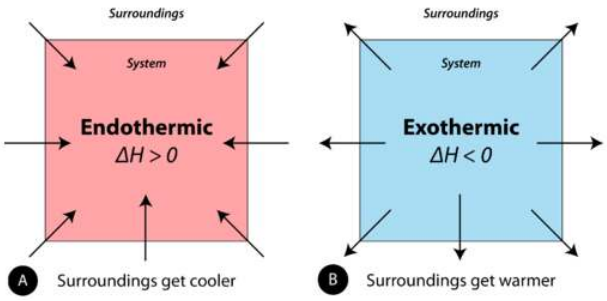


Figure 7.4.1: (A) Endothermic reaction. (B) Exothermic reaction.

Endothermic reaction: surroundings get cooler and delta H is greater than 0, Exothermic reaction: surroundings get warmer and delta H is less than 0

Endothermic Reaction: When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. Because the heat is absorbed by the system, the 177.8 kJ is written as a **reactant**. The **ΔH is positive** for an endothermic reaction.

Heat is a reactant

$$CaCO_3\,(s) + 177.8\ \text{kJ} \rightarrow CaO\,(s) + CO_2\,(g)$$

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g) \quad \Delta H = +177.8\ \text{kJ}$$

Exothermic Reaction: When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of $1\ \text{mol}$ of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation in two ways. First, the amount of heat released can be written in the **product** side of the reaction. Another way is to write the **heat of reaction** (ΔH) information with a **negative** sign, $-890.4\ \text{kJ}$.

Heat is a product

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + 890.4\ \text{kJ}$$

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) \quad \Delta H = -890.4\ \text{kJ}$$

Example 7.4.2

Is each chemical reaction exothermic or endothermic?

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

Solution

a. Because energy (213 kcal) is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.
b. Because energy (45 kcal) is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

Exercise 7.4.2

Is each chemical reaction exothermic or endothermic?

a. $H_2(g) + F_2(g) \rightarrow 2HF\,(g) + 130$ kcal
b. $2C(s) + H_2(g) + 5.3$ kcal $\rightarrow C_2H_2(g)$

Answer

a. The energy (130 kcal) is produced, hence the reaction is exothermic

b. The energy (5.3 kcal) is supplied or absorbed to react, hence, the reaction is endothermic

Energy Diagrams

Endothermic and exothermic reactions can be visually represented by *energy-level diagrams* like the ones in **Figure** 7.4.2. In endothermic reactions, the reactants have higher bond energy (stronger bonds) than the products. **Strong bonds have lower potential energy than weak bonds**. Hence, the **energy of the reactants is lower than that of the products**. This type of reaction is represented by an "uphill" energy-level diagram shown in Figure 7.4.2*A*. For an endothermic chemical reaction to proceed, the reactants must absorb energy from their environment to be converted to products.

In an exothermic reaction, the bonds in the product have higher bond energy (stronger bonds) than the reactants. In other words, the **energy of the products is lower than the energy of the reactants,** hence is energetically downhill, shown in Figure 7.4.2*B*. Energy is given off as reactants are converted to products. The energy given off is usually in the form of heat (although a few

reactions give off energy as light). In the course of an exothermic reaction, heat flows from the system to its surroundings, and thus, gets warm.

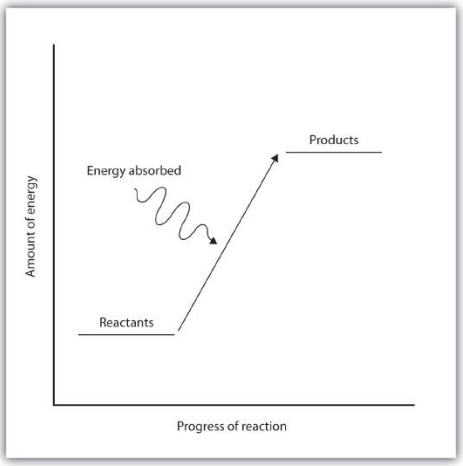


Figure 7.4.2*A*: Endothermic Reactions

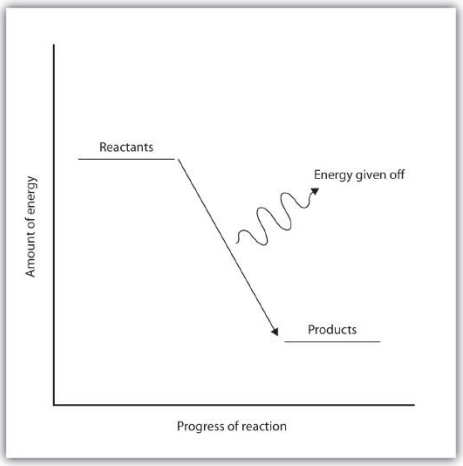


Figure 7.4.2*B*: Exothermic Reactions

Table 7.4.2: Endothermic and Exothermic Reactions

Endothermic Reactions	Exothermic Reactions
Heat is absorbed by reactants to form products.	Heat is released.
Heat is absorbed from the surroundings; as a result, the surroundings get cold.	Heat is released by the reaction to surroundings; surroundings feel hot.
ΔH_{rxn} is positive	ΔH_{rxn} is negative
The bonds broken in the reactants are stronger than the bonds formed in the products	The bonds formed in the products are stronger than the bonds broken in the reactants
The reactants are lower in energy than the products	The products are lower in energy than the reactants
Represented by an "uphill" energy diagram	Represented by an "downhill" energy diagram

Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Energy is required to break bonds. Energy is released when chemical bonds are formed because atoms become more stable.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

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7.5: 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 ($C_6H_{12}O_6$):

$$C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 6\,H_2O(\ell) + 670\ \text{kcal} \tag{7.5.1}$$

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 7.5.1. 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.

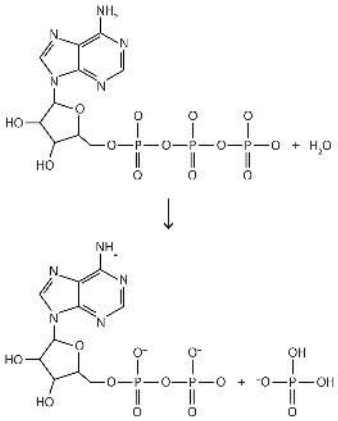


Figure 7.5.1: ATP to ADP. The conversion of ATP (top) to ADP (bottom) provides energy for the cells of the body.

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.

Key Takeaway

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

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7.6: Reversible Reactions and Chemical Equilibrium

Learning Objectives

- Define chemical equilibrium.
- Recognize chemical equilibrium as a dynamic process.

Consider the following reaction occurring in a closed container (so that no material can go in or out):

$$H_2 + I_2 \rightarrow 2HI$$

This is simply the reaction between elemental hydrogen and elemental iodine to make hydrogen iodide. The way the equation is written, we are led to believe that the reaction goes to completion, that all the H_2 and the I_2 react to make HI.

However, this is not the case because it is a **reversible reaction**, meaning it can go in either direction. As soon as there is enough product formed, the HI can react and the reverse chemical reaction occurs essentially "undoing" the first reaction:

$$2HI \rightarrow H_2 + I_2$$

Eventually, the reverse reaction proceeds so quickly that it matches the speed of the forward reaction. When that happens, the concentration of the reactants and products remains constant, there is no further change; the reaction has reached **chemical equilibrium** (sometimes just spoken as *equilibrium*; plural *equilibria*), the point at which the forward and reverse processes balance each other's progress.

Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow, like this:

$$H_2 + I_2 \rightleftharpoons 2HI$$

The double arrow implies that the reaction is going in both directions. Note that the reaction must still be balanced.

Example 7.6.1

Write the equilibrium equation that exists between calcium carbonate as a reactant and calcium oxide and carbon dioxide as products.

Solution

As this is an equilibrium situation, a double arrow is used. The equilibrium equation is written as follows:

$$CaCO_3 + \rightleftharpoons CaO + CO_2$$

Exercise 7.6.1

Write the equilibrium equation between elemental hydrogen and elemental oxygen as reactants and water as the product.

Answer

$$2H_2 + O_2 + \rightleftharpoons 2H_2O$$

One thing to note about equilibrium is that the reactions do not stop; both the forward reaction and the reverse reaction continue to occur. They both occur at the same rate, so any overall change by one reaction is canceled by the reverse reaction. We say that chemical equilibrium is *dynamic*, rather than static. Also, because both reactions are occurring simultaneously, the equilibrium can be written backward. For example, representing an equilibrium as

$$H_2 + I_2 \rightleftharpoons 2HI$$

is the same thing as representing the same equilibrium as

$$2HI \rightleftharpoons H_2 + I_2$$

The reaction must be at equilibrium for this to be the case, however.

Key Takeaways

- Chemical reactions eventually reach equilibrium, a point at which forward and reverse reactions balance each other's progress.
- Chemical equilibria are dynamic: the chemical reactions are always occurring; they just cancel each other's progress.

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7.7: Equilibrium Equations and Equilibrium Constants

Learning Objectives

- Define the equilibrium constant.
- Construct an equilibrium constant expression for a chemical reaction.

In the mid 1860s, Norwegian scientists C. M. Guldberg and P. Waage noted a peculiar relationship between the amounts of reactants and products in an equilibrium. No matter how many reactants they started with, a certain ratio of reactants and products was achieved at equilibrium. Today, we call this observation the **law of mass action**. It relates the amounts of reactants and products at equilibrium for a chemical reaction. For a general chemical reaction occurring in solution,

$$aA + bB \rightleftharpoons cC + dD$$

the **equilibrium constant**, also known as K_{eq}, is defined by the following expression:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where [A] is the molar concentration of species A at equilibrium, and so forth. The coefficients *a*, *b*, *c*, and *d* in the chemical equation become exponents in the expression for K_{eq}. The K_{eq} is a characteristic numerical value for a given reaction at a given temperature; that is, each chemical reaction has its own characteristic K_{eq}. The concentration of each reactant and product in a chemical reaction at equilibrium is *related*; the concentrations cannot be random values, but they depend on each other. The numerator of the expression for K_{eq} has the concentrations of every product (however many products there are), while the denominator of the expression for K_{eq} has the concentrations of every reactant, leading to the common *products over reactants* definition for the K_{eq}.

Let us consider a simple example. Suppose we have this equilibrium:

$$A \rightleftharpoons B$$

There is one reactant, one product, and the coefficients on each are just 1 (assumed, not written). The K_{eq} expression for this equilibrium is

$$K_{eq} = \frac{[B]}{[A]}$$

(Exponents of 1 on each concentration are understood.) Suppose the numerical value of K_{eq} for this chemical reaction is 2.0. If [B] = 4.0 M, then [A] must equal 2.0 M so that the value of the fraction equals 2.0:

$$K_{eq} = \frac{[B]}{[A]} = \frac{4.0}{2.0} = 2.0$$

By convention, the units are understood to be M and are omitted from the K_{eq} expression. Suppose [B] were 6.0 M. For the K_{eq} value to remain constant (it is, after all, called the equilibrium *constant*), then [A] would have to be 3.0 M at equilibrium:

$$K_{eq} = \frac{[B]}{[A]} = \frac{6.0}{3.0} = 2.0$$

If [A] were *not* equal to 3.0 M, the reaction would not be at equilibrium, and a net reaction would occur until that ratio was indeed 2.0. At that point, the reaction is at equilibrium, and any net change would cease. (Recall, however, that the forward and reverse reactions do not stop because chemical equilibrium is dynamic.)

The issue is the same with more complex expressions for the K_{eq}; only the mathematics become more complex. Generally speaking, given a value for the K_{eq} and all but one concentration at equilibrium, the missing concentration can be calculated.

Example 7.7.1

Given the following reaction:

$$\mathrm{H_2 + I_2 \rightleftharpoons 2\,HI} \tag{7.7.1}$$

If the equilibrium [HI] is 0.75 M and the equilibrium [H_2] is 0.20 M, what is the equilibrium [I_2] if the K_{eq} is 0.40?

Solution

We start by writing the K_{eq} expression. Using the *products over reactants* approach, the K_{eq} expression is as follows:

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

Note that [HI] is squared because of the coefficient 2 in the balanced chemical equation. Substituting for the equilibrium [H_2] and [HI] and for the given value of K_{eq}:

$$0.40 = \frac{(0.75)^2}{(0.20)[I_2]}$$

To solve for [I_2], we have to do some algebraic rearrangement: divide the 0.40 into both sides of the equation and multiply both sides of the equation by [I_2]. This brings [I_2] into the numerator of the left side and the 0.40 into the denominator of the right side:

$$[I_2] = \frac{(0.75)^2}{(0.20)(0.40)}$$

Solving,

[I_2] = 7.0 M

The concentration unit is assumed to be molarity. This value for [I_2] can be easily verified by substituting 0.75, 0.20, and 7.0 into the expression for K_{eq} and evaluating: you should get 0.40, the numerical value of K_{eq} (and you do).

Exercise 7.7.1

Given the following reaction:

$$\mathrm{H_2 + I_2 \rightleftharpoons 2\,HI} \tag{7.7.2}$$

If the equilibrium [HI] is 0.060 M and the equilibrium [I_2] is 0.90 M, what is the equilibrium [H_2] if the K_{eq} is 0.40?

Answer

0.010 M

In some types of equilibrium problems, square roots, cube roots, or even higher roots need to be analyzed to determine a final answer. Make sure you know how to perform such operations on your calculator; if you do not know, ask your instructor for assistance.

Example 7.7.2

The following reaction is at equilibrium:

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3} \tag{7.7.3}$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N_2] is 1.88 M and the equilibrium [NH_3] is 6.62 M, what is the equilibrium [H_2]?

Solution

We start by writing the K_{eq} expression from the balanced chemical equation:

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting for the known equilibrium concentrations and the K_{eq}, this becomes

$$13.7 = \frac{(6.62)^2}{(1.88)[H_2]^3}$$

Rearranging algebraically and then evaluating the numerical expression, we get

$$[H_2]^3 = \frac{(6.62)^2}{(1.88)(13.7)} = 1.7015219754$$

To solve for [H_2], we need to take the cube root of the equation. Performing this operation, we get

[H_2] = 1.19 M

You should verify that this is correct using your own calculator to confirm that you know how to do a cube root correctly.

? Exercise 7.7.2

The following reaction is at equilibrium:

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3} \tag{7.7.4}$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N_2] is 0.055 M and the equilibrium [H_2] is 1.62 M, what is the equilibrium [NH_3]?

Answer

1.79 M

The K_{eq} was defined earlier in terms of concentrations. For gas-phase reactions, the K_{eq} can also be defined in terms of the partial pressures of the reactants and products, P_i. For the gas-phase reaction

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

the pressure-based equilibrium constant, K_P, is defined as follows:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where P_A is the partial pressure of substance A at equilibrium in atmospheres, and so forth. As with the concentration-based equilibrium constant, the units are omitted when substituting into the expression for K_P.

✓ Example 7.7.3

What is the K_P for this reaction, given the equilibrium partial pressures of 0.664 atm for NO_2 and 1.09 for N_2O_4?

$$\mathrm{2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)} \tag{7.7.5}$$

Solution

Write the K_P expression for this reaction:

$$K_P = \frac{P_{N_2O_4}}{P_{NO_2}^2}$$

Then substitute the equilibrium partial pressures into the expression and evaluate:

$$K_P = \frac{(1.09)}{(0.664)^2} = 2.47$$

Exercise 7.7.3

What is the K_P for this reaction, given the equilibrium partial pressures of 0.44 atm for H_2, 0.22 atm for Cl_2, and 2.98 atm for HCl?

$$H_2 + Cl_2 \rightleftharpoons 2\,HCl \tag{7.7.6}$$

Answer

91.7

There is a simple relationship between K_{eq} (based on concentration units) and K_P (based on pressure units):

$$K_P = K_{eq} \cdot (RT)^{\Delta n}$$

where R is the ideal gas law constant (in units of L·atm/mol·K), T is the absolute temperature, and Δn is the change in the number of moles of gas in the balanced chemical equation, defined as $n_{gas,prods} - n_{gas,rcts}$. Note that this equation implies that if the number of moles of gas are the same in reactants and products, $K_{eq} = K_P$.

Example 7.7.4

What is the K_P at 25°C for this reaction if the K_{eq} is 4.2×10^{-2}?

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \tag{7.7.7}$$

Solution

Before we use the relevant equation, we need to do two things: convert the temperature to kelvins and determine Δn. Converting the temperature is easy:

$T = 25 + 273 = 298$ K

To determine the change in the number of moles of gas, take the number of moles of gaseous products and subtract the number of moles of gaseous reactants. There are 2 mol of gas as product and 4 mol of gas of reactant:

$\Delta n = 2 - 4 = -2$ mol

Note that Δn is negative. Now we can substitute into our equation, using $R = 0.08205$ L·atm/mol·K. The units are omitted for clarity:

$K_P = (4.2 \times 10^{-2})(0.08205)(298)^{-2}$

Solving,

$K_P = 7.0 \times 10^{-5}$

Exercise 7.7.4 .

What is the K_P at 25°C for this reaction if the K_{eq} is 98.3?,-

$$I_2\,(g) \rightleftharpoons 2\,I\,(g) \tag{7.7.8}$$

Answer

2.40×10^{3}

Finally, we recognize that many chemical reactions involve substances in the solid or liquid phases. For example, a particular chemical reaction is represented as follows:

$$2\,NaHCO_3\,(s) \rightleftharpoons Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l) \tag{7.7.9}$$

This chemical equation includes all three phases of matter. This kind of equilibrium is called a **heterogeneous equilibrium** because there is more than one phase present.

The rule for heterogeneous equilibria is as follows: *Do not include the concentrations of pure solids and pure liquids in* K_{eq} *expressions.* Only partial pressures for gas-phase substances or concentrations in solutions are included in the expressions of equilibrium constants. As such, the equilibrium constant expression for this reaction would simply be

$$K_P = P_{CO_2}$$

because the two solids and one liquid would not appear in the expression.

Key Takeaways

- Every chemical equilibrium can be characterized by an equilibrium constant, known as K_{eq}.
- The K_{eq} and K_P expressions are formulated as amounts of products divided by amounts of reactants; each amount (either a concentration or a pressure) is raised to the power of its coefficient in the balanced chemical equation.
- Solids and liquids do not appear in the expression for the equilibrium constant.

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7.8: Le Chatelier’s Principle- The Effect of Changing Conditions on Equilibria

Learning Objectives

- Define *Le Chatelier's principle*.
- Predict the direction of shift for an equilibrium under stress.

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called **Le Chatelier's principle**: If an equilibrium is stressed, then the reaction shifts to reduce the stress.

Effect of Changes in Concentration

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

Example 7.8.1

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In which direction—toward reactants or toward products-—does the reaction shift if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift toward products to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

Exercise 7.8.1

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answers

1. toward reactants
2. toward reactants

It is worth noting that when reactants or products are added or removed, *the value of the* K_{eq} *does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

Effect of Changes in Pressure and Temperature

How does an equilibrium react to a change in *pressure*? Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

Example 7.8.2

What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts toward the products side.

Exercise 7.8.2

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

Answer

Reaction shifts toward reactants.

What is the effect of *temperature* changes on an equilibrium? It depends on whether the reaction is endothermic or exothermic. Recall that *endothermic* means that energy is absorbed by a chemical reaction, while *exothermic* means that energy is given off by the reaction. As such, energy can be thought of as a reactant or a product, respectively, of a reaction:

endothermic reaction: energy + reactants → products

exothermic reaction: reactants → products + energy

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for exothermic reactions), and the equilibrium shifts accordingly.

Example 7.8.3

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

? Exercise 7.8.3

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

Answer

Equilibrium shifts toward reactants.

In the case of temperature, the value of the equilibrium has changed because the K_{eq} is dependent on temperature. That is why equilibria shift with changes in temperature.

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds. However, a catalyst does not affect the extent or position of a reaction at equilibrium. It helps a reaction achieve equilibrium faster.

✔ Chemistry is Everywhere: Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?



Figure 7.8.1 Garden Equilibria © Thinkstock. This species of hydrangea has flowers that can be either red or blue. Why the color difference?

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H^+ or OH^- ions that affect the color of the flowers. Rather, it is the presence of aluminum that causes the color change.

The solubility of aluminum in soil, and the ability of plants to absorb it, is dependent upon the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue, as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

Key Takeaways

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- The direction of shift can be predicted for changes in concentrations, temperature, or pressure.

- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

Exercise 7.8.1

1. Define *Le Chatelier's principle*.
2. What is meant by a stress? What are some of the ways an equilibrium can be stressed?
3. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + I_2(s) + 53kJ \rightleftharpoons 2HI(g)$$

   a. decreased temperature
   b. increased pressure
   c. removal of HI

4. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g) + 546kJ$$

   a. increased temperature
   b. addition of H_2
   c. decreased pressure

5. Given this equilibrium, predict the direction of shift for each stress.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 196kJ$$

   a. removal of SO_3
   b. addition of O_2
   c. decreased temperature

6. Given this equilibrium, predict the direction of shift for each stress.

$$CO_2(g) + C(s) + 171kJ \rightleftharpoons 2CO(g)$$

   a. addition of CO
   b. increased pressure
   c. addition of a catalyst

7. The synthesis of NH_3 uses this chemical reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92kJ$$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH_3.

8. The synthesis of $CaCO_3$ uses this chemical reaction.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + 180kJ$$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of $CaCO_3$.

Answers

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.
2.
3. a. toward reactants

- toward reactants
- toward products
-
- a. toward products
  b. toward products

c. toward products

-
- increased pressure, decreased temperature, removal of NH_3

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7.E: Energy and Chemical Processes (Exercises)

7.1: Energy and Its Units

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.

Exercises

1. Define *energy*.
2. What is heat?
3. What is the relationship between a calorie and a joule? Which unit is larger?
4. What is the relationship between a calorie and a kilocalorie? Which unit is larger?
5. Express 1,265 cal in kilocalories and in joules.
6. Express 9,043.3 J in calories and in kilocalories.
7. One kilocalorie equals how many kilojoules?
8. One kilojoule equals how many kilocalories?
9. Many nutrition experts say that an average person needs 2,000 Cal per day from his or her diet. How many joules is this?
10. Baby formula typically has 20.0 Cal per ounce. How many ounces of formula should a baby drink per day if the RDI is 850 Cal?

Answers

1. Energy is the ability to do work.
2. Heat is a form of enery (thermal) that can be transferred from one object to another.
3. 1 cal = 4.184 J; the calorie is larger.
4. 1 kilocalorie(1 Cal) = 1000 cal; the kcal is larger.
5. 1.265 kcal; 5,293 J
6. 2161.4 cal; 2.1614 kcal
7. 1 kcal = 4.184 kJ
8. 1 kJ = 0.239 kcal
9. 8.4×10^6 J
10. 42.5 oz

7.2: Heat and Temperature

Concept Review Exercise

1. Describe the relationship between heat transfer and the temperature change of an object.
2. Describe what happens when two objects that have different temperatures come into contact with one another.

Answer

1. Heat is equal to the product of the mass, the change in temperature, and a proportionality constant called the specific heat.

2. 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.

Exercises

1. The melting point of mercury is −38.84°C. Convert this value to degrees Fahrenheit and Kelvin.

2. A pot of water is set on a hot burner of a stove. What is the direction of heat flow?

3. Some uncooked macaroni is added to a pot of boiling water. What is the direction of heat flow?

4. How much energy in calories is required to heat 150 g of H_2O from 0°C to 100°C?

5. How much energy in calories is required to heat 125 g of Fe from 25°C to 150°C?

6. If 250 cal of heat were added to 43.8 g of Al at 22.5°C, what is the final temperature of the aluminum?

7. If 195 cal of heat were added to 33.2 g of Hg at 56.2°C, what is the final temperature of the mercury?

8. A sample of copper absorbs 145 cal of energy, and its temperature rises from 37.8°C to 41.7°C. What is the mass of the copper?

9. A large, single crystal of sodium chloride absorbs 98.0 cal of heat. If its temperature rises from 22.0°C to 29.7°C, what is the mass of the NaCl crystal?

10. If 1.00 g of each substance in Table 7.2.1 were to absorb 100 cal of heat, which substance would experience the largest temperature change?

11. If 1.00 g of each substance in Table 7.2.1 were to absorb 100 cal of heat, which substance would experience the smallest temperature change?

12. Determine the heat capacity of a substance if 23.6 g of the substance gives off 199 cal of heat when its temperature changes from 37.9°C to 20.9°C.

13. What is the heat capacity of gold if a 250 g sample needs 133 cal of energy to increase its temperature from 23.0°C to 40.1°C?

Answers

1. -37.91°F and 234.31 K

2. Heat flows into the pot of water.

3. Heat flows to the macaroni.

4. 15,000 cal

5. 1,690 cal

6. 49.0°C

7. 234°C

8. 404 g

9. 61 g

10. Mercury would experience the largest temperature change.

11. hydrogen (H_2)

12. 0.496 cal/g•°C

13. 0.031 cal/g•°C

7.3: Phase Changes

Concept Review Exercises

1. Explain what happens when heat flows into or out of a substance at its melting point or boiling point.
2. How does the amount of heat required for a phase change relate to the mass of the substance?
3. What is the direction of heat transfer in boiling water?
4. What is the direction of heat transfer in freezing water?
5. What is the direction of heat transfer in sweating?

Answers

1. The energy goes into changing the phase, not the temperature.

2. The amount of heat is a constant per gram of substance.

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

4. 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.

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

Exercises

1. How much energy is needed to melt 43.8 g of Au at its melting point of 1,064°C?
2. How much energy is given off when 563.8 g of NaCl solidifies at its freezing point of 801°C?
3. What mass of ice can be melted by 558 cal of energy?
4. How much ethanol (C_2H_5OH) in grams can freeze at its freezing point if 1,225 cal of heat are removed?
5. What is the heat of vaporization of a substance if 10,776 cal are required to vaporize 5.05 g? Express your final answer in joules per gram.
6. If 1,650 cal of heat are required to vaporize a sample that has a heat of vaporization of 137 cal/g, what is the mass of the sample?
7. What is the heat of fusion of water in calories per mole?
8. What is the heat of vaporization of benzene (C_6H_6) in calories per mole?
9. What is the heat of vaporization of gold in calories per mole?
10. What is the heat of fusion of iron in calories per mole?

Answers

1. 670 cal

2. 69,630 cal

3. 6.98 g

4. 27.10 g

5. 8,930 J/g

6. 12.0 g

7. 1,440 cal/mol

8. 7,350 cal/mol

9. 80,600 cal/mol

10. 3,530 cal/mol

7.4: Bond Energies and Chemical Reactions

Concept Review Exercises

1. What is the connection between energy and chemical bonds?
2. Why does energy change during the course of a chemical reaction?
3. Two different reactions are performed in two identical test tubes. In reaction A, the test tube becomes very warm as the reaction occurs. In reaction B, the test tube becomes cold. Which reaction is endothermic and which is exothermic? Explain.
4. Classify "burning paper" as endothermic or exothermic processes.

Answers

1. Chemical bonds have a certain energy that is dependent on the elements in the bond and the number of bonds between the atoms.
2. Energy changes because bonds rearrange to make new bonds with different energies.
3. Reaction A is exothermic because heat is leaving the system making the test tube feel hot. Reaction B is endothermic because heat is being absorbed by the system making the test tube feel cold.
4. "Burning paper" is exothermic because burning (also known as combustion) releases heat

Exercises

1. Using the data in Table 7.4.1, calculate the energy of one C–H bond (as opposed to 1 mol of C–H bonds). Recall that 1 mol = 6.022×10^{23} C–H bonds

2. Using the data in Table 7.4.1, calculate the energy of one C=C bond (as opposed to 1 mol of C=C bonds). Recall that 1 mol = 6.022×10^{23} C=C bonds

3. Is a bond-breaking process exothermic or endothermic?

4. Is a bond-making process exothermic or endothermic?

5. Is each chemical reaction exothermic or endothermic?

   a. $2SnCl_2(s) + 33\ kcal \rightarrow Sn(s) + SnCl_4(s)$
   b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213\ kcal$

6. Is each chemical reaction exothermic or endothermic?

   a. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) + 137\ kJ$
   b. $C(s, graphite) + 1.9\ kJ \rightarrow C(s, diamond)$

Answers

1. 1.661×10^{-19} cal

2. 2.408×10^{-19} cal

3. endothermic

4. exothermic

5.

   a. endothermic

   b. exothermic

6.

a. exothermic

b. endothermic

7.5: The Energy of Biochemical Reactions

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

Exercises

1. An 8 oz serving of whole milk has 8.0 g of fat, 8.0 g of protein, and 13 g of carbohydrates. Approximately how many kilocalories does it contain?
2. A serving of potato chips has 160 kcal. If the chips have 15 g of carbohydrates and 2.0 g of protein, about how many grams of fat are in a serving of potato chips?
3. The average body temperature of a person is 37°C, while the average surrounding temperature is 22°C. Is overall human metabolism exothermic or endothermic?
4. Cold-blooded animals absorb heat from the environment for part of the energy they need to survive. Is this an exothermic or an endothermic process?
5. If the reaction ATP → ADP gives off 7.5 kcal/mol, then the reverse process, ADP → ATP requires 7.5 kcal/mol to proceed. How many moles of ADP can be converted to ATP using the energy from 1 serving of potato chips (see Exercise 2)?
6. If the oxidation of glucose yields 670 kcal of energy per mole of glucose oxidized, how many servings of potato chips (see Exercise 2) are needed to provide the same amount of energy?

Answers

1. 156 kcal
2. 10.2 g
3. exothermic
4. endothermic
5. 21.3 mol
6. 4.2 servings

Additional Exercises

1. Sulfur dioxide (SO_2) is a pollutant gas that is one cause of acid rain. It is oxidized in the atmosphere to sulfur trioxide (SO_3), which then combines with water to make sulfuric acid (H_2SO_4).
   a. Write the balanced reaction for the oxidation of SO_2 to make SO_3. (The other reactant is diatomic oxygen.)
   b. When 1 mol of SO_2 reacts to make SO_3, 23.6 kcal of energy are given off. If 100 lb (1 lb = 454 g) of SO_2 were converted to SO_3, what would be the total energy change?
2. Ammonia (NH_3) is made by the direct combination of H_2 and N_2 gases according to this reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + 22.0 \text{ kcal}$$

   a. Is this reaction endothermic or exothermic?
   b. What is the overall energy change if 1,500 g of N_2 are reacted to make ammonia?

3. A 5.69 g sample of iron metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H_2O at 22.6°C. Assuming that the water gained all the heat lost by the iron, what is the final temperature of the H_2O and Fe?
4. A 5.69 g sample of copper metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H_2O at 22.6°C. Assuming that the water gained all the heat lost by the copper, what is the final temperature of the H_2O and Cu?
5. When 1 g of steam condenses, 540 cal of energy is released. How many grams of ice can be melted with 540 cal?
6. When 1 g of water freezes, 79.9 cal of energy is released. How many grams of water can be boiled with 79.9 cal?
7. The change in energy is +65.3 kJ for each mole of calcium hydroxide [$Ca(OH)_2$] according to the following reaction:

$$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$$

How many grams of $Ca(OH)_2$ could be reacted if 575 kJ of energy were available?

8. The thermite reaction gives off so much energy that the elemental iron formed as a product is typically produced in the liquid state:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(\ell) + 204 \text{ kcal}$$

How much heat will be given off if 250 g of Fe are to be produced?

9. A normal adult male requires 2,500 kcal per day to maintain his metabolism.
    a. Nutritionists recommend that no more than 30% of the calories in a person's diet come from fat. At 9 kcal/g, what is the maximum mass of fat an adult male should consume daily?
    b. At 4 kcal/g each, how many grams of protein and carbohydrates should an adult male consume daily?
10. A normal adult male requires 2,500 kcal per day to maintain his metabolism.
    a. At 9 kcal/g, what mass of fat would provide that many kilocalories if the diet was composed of nothing but fats?
    b. At 4 kcal/g each, what mass of protein and/or carbohydrates is needed to provide that many kilocalories?
11. The volume of the world's oceans is approximately 1.34×10^{24} cm^3.
    a. How much energy would be needed to increase the temperature of the world's oceans by 1°C? Assume that the heat capacity of the oceans is the same as pure water.
    b. If Earth receives 6.0×10^{22} J of energy per day from the sun, how many days would it take to warm the oceans by 1°C, assuming all the energy went into warming the water?
12. Does a substance that has a small specific heat require a small or large amount of energy to change temperature? Explain.
13. Some biology textbooks represent the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and phosphate ions as follows:

$$ATP \rightarrow ADP + \text{phosphate} + \text{energy}$$

What is wrong with this reaction?

14. Assuming that energy changes are additive, how much energy is required to change 15.0 g of ice at −15°C to 15.0 g of steam at 115°C? (Hint: you will have five processes to consider.)

Answers

1.
    a. $2SO_2 + O_2 \rightarrow 2SO_3$
    b. 16,700 kcal
2.
    a. exothermic
    b. 1177 kcal
3. about 23.1°C

4. about 23.0°C

5. 6.76 g

6. 0.148 g

7. 652 g

8. 457 kcal

9.

   a. 83.3 g
   b. 438 g

10.

   a. 278 g
   b. 625 g

11.

   a. 1.34×10^{24} cal
   b. 93 days

12. A substance with **smaller specific heat** requires **less energy** per unit of mass to raise its temperature,

13. A reactant is missing: H_2O is missing.

14. Total energy = 11,019 cal

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7.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). The amount of heat gained or lost when the temperature of an object changes can be related to its mass and a constant called the **specific heat** of the substance.

The transfer of energy can also cause a substance to change from one phase to another. During the transition, called a **phase change**, heat is either added or lost. Despite the fact that heat is going into or coming out of a substance during a phase change, the temperature of the substance does not change until the phase change is complete; that is, phase changes are **isothermal**. Analogous to specific heat, a constant called the **heat of fusion** of a substance describes how much heat must be transferred for a substance to melt or solidify (that is, to change between solid and liquid phases), while the **heat of vaporization** describes the amount of heat transferred in a boiling or condensation process (that is, to change between liquid and gas phases).

Every chemical change is accompanied by an energy change. This is because the interaction between atoms bonding to each other has a certain **bond energy**, the energy required to break the bond (called **lattice energy** for ionic compounds), and the bond energies of the reactants will not be the same as the bond energies of the products. 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

8: Solids, Liquids, and Gases

Most of us are familiar with the three phases of matter: solid, liquid, and gas. Indeed, we addressed the energy changes involved in phase changes. The substance we are probably most familiar with has those three phases: water. In everyday life, we commonly come in contact with water as a solid (ice), as a liquid, and as a gas (steam). All we have to do is change the conditions of the substance—typically temperature—and we can change the phase from solid to liquid to gas and back again. Under the proper conditions of temperature and pressure, many substances—not only water—can experience the three different phases. An understanding of the phases of matter is important for our understanding of all matter. In this chapter, we will explore the three phases of matter.

8.0: Prelude to Solids, Liquids, and Gases

8.1: Intermolecular Interactions

8.2: Solids and Liquids

8.3: Gases and Pressure

8.4: Gas Laws

8.E: Solids, Liquids, and Gases (Exercises)

8.S: Solids, Liquids, and Gases (Summary)

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8.0: 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 8.0.1: 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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8.1: 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 8.1.1 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 8.1.1: 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.**

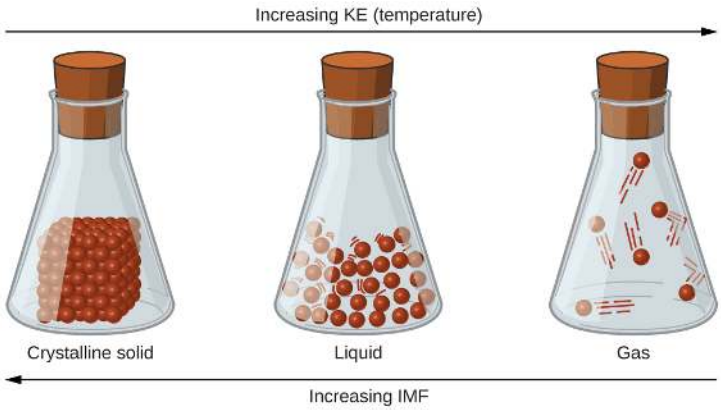


Figure 8.1.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.) (CC BY 4.0; OpenStax)

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 8.1.2). 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.

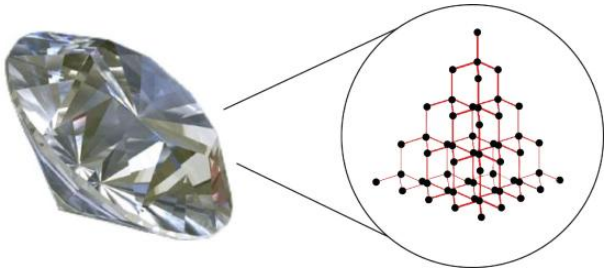


Figure 8.1.2: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state. Source: Photo © Thinkstock

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 8.1.3) is an example of a substance whose particles experience ionic interactions (Table 8.1.1). These attractive forces are sometimes referred to as ion-ion interactions.

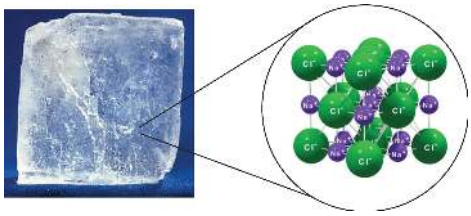


Figure 8.1.3: Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock

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.***

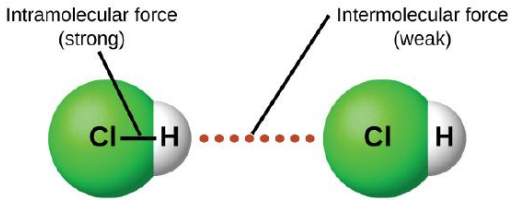


Figure 8.1.4: **Intramolecular** forces keep a molecule intact. **Intermolecular** forces hold multiple molecules together and determine many of a substance's properties. (CC BY 4.0; OpenStax)

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 8.1.5: 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− [illegible] 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*.

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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 8.1.6).

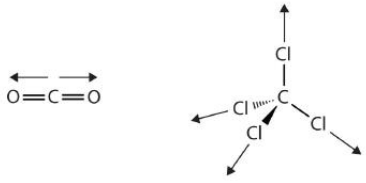


Figure 8.1.6: Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

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 8.1.7.

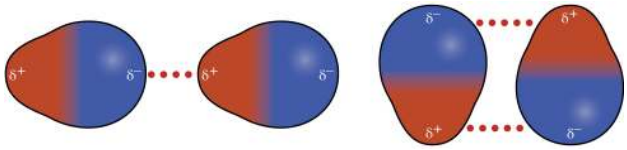


Figure 8.1.7: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

Two pairs of molecules are shown where each molecule has one larger blue side labeled “delta sign, negative sign” and a smaller red side labeled “delta sign, positive sign. In the first pair, the red sides of the two molecules both face to the left and the blue side to the right. A horizontal dotted line lies in between the two. In the second pair, the molecules face up and down, with the red and blue ends aligning. A horizontal dotted line lies between the red and blue ends facing upward and another lies between the red and blue ends facing downward.

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.

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Example 8.1.1

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.

8.1.1 Exercise

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

covalently bonded, is partially 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 8.1.8 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.

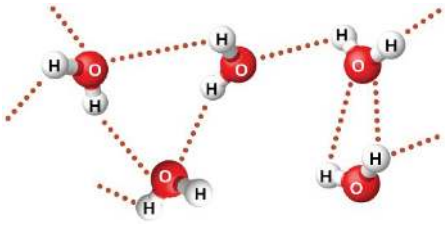


Figure 8.1.8: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.
Five water molecules are shown near one another, but not touching. A dotted line lies between many of the hydrogen atoms on one molecule and the oxygen atom on another molecule.

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 8.1.9 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:

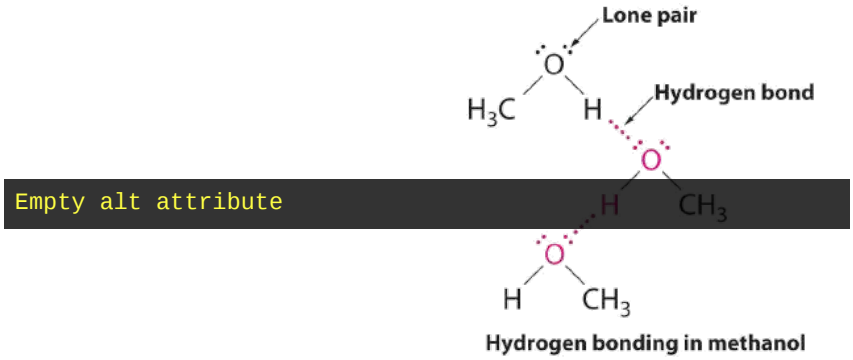


Figure 8.1.9: Methanol molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

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.

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Exercise 8.1.2

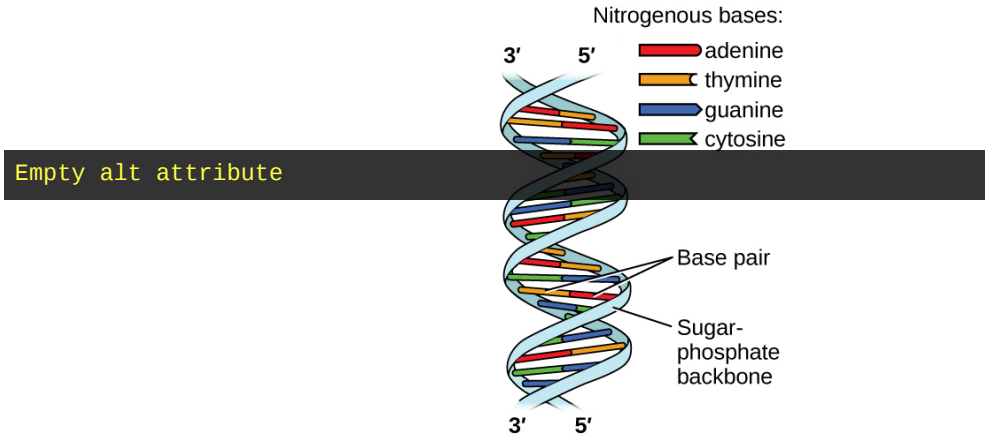
Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

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 8.1.10.



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Figure 8.1.10: 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 8.1.11

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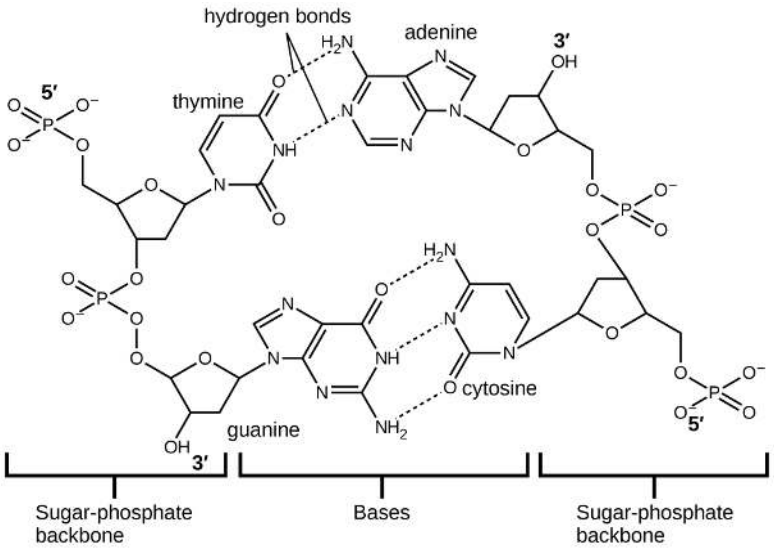


Figure 8.1.11: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

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 8.1.2: **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 8.1.3

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.

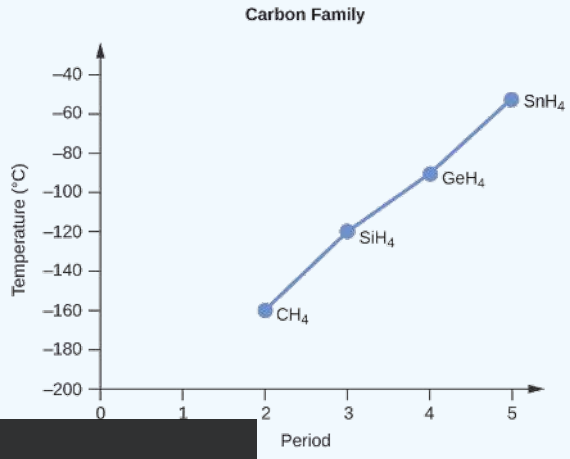
Solution

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Applying the principles discussed 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:



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A line graph, titled “Carbon Family,” is shown where the y-axis is labeled “Temperature, (degree sign C)” and has values of “negative 200” to “negative 40” from bottom to top in increments of 20. The x-axis is labeled “Period” and has values of “0” to “5” in increments of 1. The first point on the graph is labeled “C H subscript 4” and is at point “2, negative 160.” The second point on the graph is labeled “S i H subscript 4” and is at point “3, negative 120” while the third point on the graph is labeled “G e H subscript 4” and is at point “4, negative 100.” The fourth point on the graph is labeled “S n H subscript 4” and is at point “5, negative 60.”

8.1.3Exercise

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.

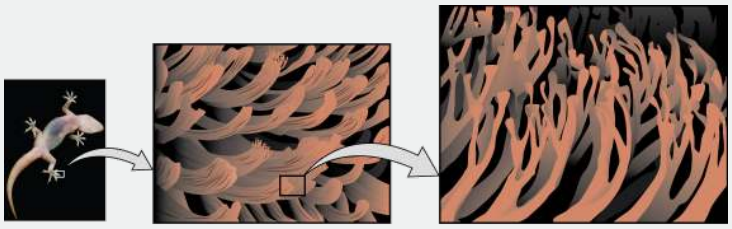


Figure 8.1.12: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)*

Three figures are shown. The first is a photo of the bottom of a gecko's foot. The second is bigger version which shows the setae. The third is a bigger version of the setae and shows the spatulae.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.1.12, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar Cl_2 has a higher boiling point than polar HCl.

Table 8.1.3: Intermolecular Forces and Boiling Points

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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 8.1.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

Exercise 8.1.4

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

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
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- 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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8.2: 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 8.2.1: 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 8.2.1. 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 8.2.2: 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.

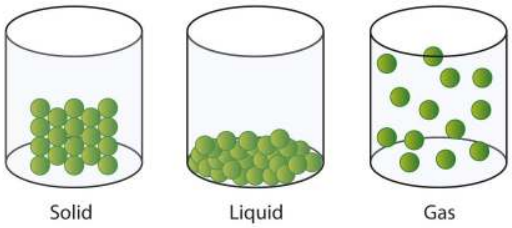


Figure 8.2.3: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

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 8.2.3 shows the differences among solids, liquids, and gases at the molecular level, while Table 8.2.1 lists the different characteristics of these states.

Table 8.2.1: 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 8.2.1

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 8.2.1

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.

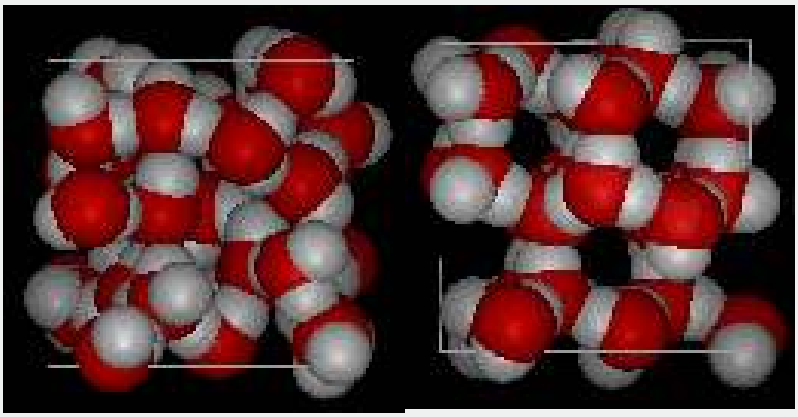


Figure 8.2.4: Three-dimensional views of a typical local structure of liquid water (left) and ice (right).

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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8.3: Gases and Pressure

Learning Objectives

- To describe the gas phase.

The gas phase is unique among the three states of matter in that there are some simple models we can use to predict the physical behavior of all gases—independent of their identities. We cannot do this for the solid and liquid states. In fact, the development of this understanding of the behavior of gases represents the historical dividing point between alchemy and modern chemistry. Initial advances in the understanding of gas behavior were made in the mid 1600s by Robert Boyle, an English scientist who founded the Royal Society (one of the world's oldest scientific organizations).

How is it that we can model all gases independent of their chemical identity? The answer is in a group of statements called the kinetic theory of gases:

- Gases are composed of tiny particles that are separated by large distances.
- Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container.
- The velocity of gas particles is related to the temperature of a gas.
- Gas particles do not experience any force of attraction or repulsion with each other.

Did you notice that none of these statements relates to the identity of the gas? This means that all gases should behave similarly. A gas that follows these statements perfectly is called an *ideal gas*. Most gases show slight deviations from these statements and are called *real gases*. However, the existence of real gases does not diminish the importance of the kinetic theory of gases.

One of the statements of the kinetic theory mentions collisions. As gas particles are constantly moving, they are also constantly colliding with each other and with the walls of their container. There are forces involved as gas particles bounce off the container walls (Figure 8.3.1). The force generated by gas particles divided by the area of the container walls yields pressure. Pressure is a property we can measure for a gas, but we typically do not consider pressure for solids or liquids.

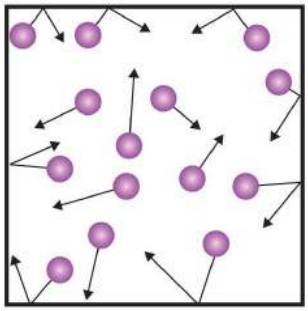


Figure 8.3.1: Gas Pressure. Pressure is what results when gas particles rebound off the walls of their container.

The basic unit of pressure is the newton per square meter (N/m^2). This combined unit is redefined as a pascal (Pa). One pascal is not a very large amount of pressure. A more useful unit of pressure is the bar, which is 100,000 Pa (1 bar = 100,000 Pa). Other common units of pressure are the atmosphere (atm), which was originally defined as the average pressure of Earth's atmosphere at sea level; and mmHg (millimeters of mercury), which is the pressure generated by a column of mercury 1 mm high. The unit millimeters of mercury is also called a torr, named after the Italian scientist Evangelista Torricelli, who invented the barometer in the mid-1600s. A more precise definition of atmosphere, in terms of torr, is that there are exactly 760 torr in 1 atm. A bar equals 1.01325 atm. Given all the relationships between these pressure units, the ability to convert from one pressure unit to another is a useful skill.

Example 8.3.1: Converting Pressures

Write a conversion factor to determine how many atmospheres are in 1,547 mmHg.

Solution

Because 1 mmHg equals 1 torr, the given pressure is also equal to 1,547 torr. Because there are 760 torr in 1 atm, we can use this conversion factor to do the mathematical conversion:

$$1,547 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.04 \text{ atm}$$

Note how the torr units cancel algebraically.

? Exercise 8.3.1: Converting Pressures

Write a conversion factor to determine how many millimeters of mercury are in 9.65 atm.

Answer

$$9.65 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 7,334 \text{ mmHg}.$$

The kinetic theory also states that there is no interaction between individual gas particles. Although we know that there are, in fact, intermolecular interactions in real gases, the kinetic theory assumes that gas particles are so far apart that the individual particles don't "feel" each other. Thus, we can treat gas particles as tiny bits of matter whose identity isn't important to certain physical properties.

Key Takeaway

- The gas phase has certain general properties characteristic of that phase.

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8.4: Gas Laws

Learning Objectives

- To predict the properties of gases using the gas laws.

Experience has shown that several properties of a gas can be related to each other under certain conditions. The properties are pressure (*P*), volume (*V*), temperature (*T*, in kelvins), and amount of material expressed in moles (*n*). What we find is that a sample of gas cannot have any random values for these properties. Instead, only certain values, dictated by some simple mathematical relationships, will occur.

Boyle's Law

The first simple relationship, referred to as a gas law, is between the pressure of a gas and its volume. If the amount of gas in a sample and its temperature are kept constant, then as the pressure of a gas is increased, the volume of the gas decreases proportionately. Mathematically, this is written as

$$\mathrm{P} \propto \frac{1}{\mathrm{V}}$$

where the "∝" symbol means "is proportional to." This is one form of Boyle's law, which relates the pressure of a gas to its volume.

A more useful form of Boyle's law involves a change in conditions of a gas. For a given amount of gas at a constant temperature, if we know the initial pressure and volume of a gas sample and the pressure or volume changes, we can calculate what the new volume or pressure will be. That form of Boyle's law is written

$$P_i V_i = P_f V_f \tag{8.4.1}$$

where the subscript i refers to initial conditions and the subscript f refers to final conditions.

To use 8.4.1, you need to know any three of the variables so that you can algebraically calculate the fourth variable. Also, the pressure quantities must have the same units, as must the two volume quantities. If the two similar variables don't have the same variables, one value must be converted to the other value's unit.

Example 8.4.1: Increasing Pressure in a Gas

What happens to the volume of a gas if its pressure is increased? Assume all other conditions remain the same.

Solution

If the pressure of a gas is increased, the volume decreases in response.

Exercise 8.4.1: Increasing Volume in a Gas

What happens to the pressure of a gas if its volume is increased? Assume all other conditions remain the same.

Answer

If the volume of a gas is increased, the pressure decreases.

Example 8.4.2: Gas Compression

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is reduced to 0.987 atm? Assume that the amount and the temperature of the gas remain constant.

Solution

The key in problems like this is to be able to identify which quantities represent which variables from the relevant equation. The way the question is worded, you should be able to tell that 1.56 atm is P_i, 7.02 L is V_i, and 0.987 atm is P_f. What we are looking for is the final volume—V_f. Therefore, substituting these values into $P_iV_i = P_fV_f$:

$$(1.56 \text{ atm})(7.02 \text{ L}) = (0.987 \text{ atm}) \times V_f$$

The expression has atmospheres on both sides of the equation, so they cancel algebraically:

$$(1.56)(7.02 \text{ L}) = (0.987) \times V_f$$

Now we divide both sides of the expression by 0.987 to isolate V_f, the quantity we are seeking:

$$\frac{(1.56)(7.02 \text{ L})}{0.987} = \text{V}_\text{f}$$

Performing the multiplication and division, we get the value of V_f, which is 11.1 L. The volume increases. This should make sense because the pressure decreases, so pressure and volume are inversely related.

? Exercise 8.4.2

If a sample of gas has an initial pressure of 3.66 atm and an initial volume of 11.8 L, what is the final pressure if the volume is reduced to 5.09 L? Assume that the amount and the temperature of the gas remain constant.

Answer

8.48 atm

If the units of similar quantities are not the same, one of them must be converted to the other quantity's units for the calculation to work out properly. It does not matter which quantity is converted to a different unit; the only thing that matters is that the conversion and subsequent algebra are performed properly. The following example illustrates this process.

✔ Example 8.4.3

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is changed to 1,775 torr? Does the answer make sense? Assume that the amount and the temperature of the gas remain constant.

Solution

This example is similar to Example 8.4.2, except now the final pressure is expressed in torr. For the math to work out properly, one of the pressure values must be converted to the other unit. Let us change the initial pressure to torr:

$$1.56 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 1,190 \text{ torr}$$

Now we can use Boyle's law:

$$(1{,}190 \text{ torr})(7.02 \text{ L}) = (1{,}775 \text{ torr}) \times V_f$$

Torr cancels algebraically from both sides of the equation, leaving

$$(1{,}190)(7.02 \text{ L}) = (1{,}775) \times V_f$$

Now we divide both sides of the equation by 1,775 to isolate V_f on one side. Solving for the final volume,

$$\text{V}_\text{f} = \frac{(1,190)(7.02 \text{ L})}{1,775} = 4.71 \text{ L}$$

Because the pressure increases, it makes sense that the volume decreases.

The answer for the final volume is essentially the same if we converted the 1,775 torr to atmospheres: $1,775 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.336 \text{ atm}$. Using Boyle's law: (1.56 atm)(7.02 L) = (2.335 atm) × V_f; $\text{V}_\text{f} = \frac{(1.56 \text{ atm})(7.02 \text{ L})}{2.336 \text{ atm}} = 4.69 \text{ L}$.

Exercise 8.4.3

If a sample of gas has an initial pressure of 375 torr and an initial volume of 7.02 L, what is the final pressure if the volume is changed to 4,577 mL? Does the answer make sense? Assume that amount and the temperature of the gas remain constant.

Answer

575 torr

To Your Health: Breathing

Breathing certainly is a major contribution to your health! Without breathing, we could not survive. Curiously, the act of breathing itself is little more than an application of Boyle's law.

The lungs are a series of ever-narrowing tubes that end in a myriad of tiny sacs called alveoli. It is in the alveoli that oxygen from the air transfers to the bloodstream and carbon dioxide from the bloodstream transfers to the lungs for exhalation. For air to move in and out of the lungs, the pressure inside the lungs must change, forcing the lungs to change volume—just as predicted by Boyle's law.

The pressure change is caused by the diaphragm, a muscle that covers the bottom of the lungs. When the diaphragm moves down, it expands the size of our lungs. When this happens, the air pressure inside our lungs decreases slightly. This causes new air to rush in, and we inhale. The pressure decrease is slight—only 3 torr, or about 0.4% of an atmosphere. We inhale only 0.5–1.0 L of air per normal breath.

Exhaling air requires that we relax the diaphragm, which pushes against the lungs and slightly decreases the volume of the lungs. This slightly increases the pressure of the air in the lungs, and air is forced out; we exhale. Only 1–2 torr of extra pressure is needed to exhale. So with every breath, our own bodies are performing an experimental test of Boyle's law.

Charles's Law

Another simple gas law relates the volume of a gas to its temperature. Experiments indicate that as the temperature of a gas sample is increased, its volume increases as long as the pressure and the amount of gas remain constant. The way to write this mathematically is

$$\mathrm{V} \propto T$$

At this point, the concept of temperature must be clarified. Although the Kelvin scale is the preferred temperature scale, the Celsius scale is also a common temperature scale used in science. The Celsius scale is based on the melting and boiling points of water and is actually the common temperature scale used by most countries around the world (except for the United States, which still uses the Fahrenheit scale). The value of a Celsius temperature is directly related to its Kelvin value by a simple expression:

$$\text{Kelvin temperature} = \text{Celsius temperature} + 273$$

Thus, it is easy to convert from one temperature scale to another.

The Kelvin scale is sometimes referred to as the absolute scale because the zero point on the Kelvin scale is at absolute zero, the coldest possible temperature. On the other temperature scales, absolute zero is −260°C or −459°F.

The expression relating a gas volume to its temperature begs the following question: to which temperature scale is the volume of a gas related? The answer is that gas volumes are directly related to the *Kelvin temperature*. Therefore, the temperature of a gas sample should always be expressed in (or converted to) a Kelvin temperature.

Example 8.4.4: Increasing Temperature

What happens to the volume of a gas if its temperature is decreased? Assume that all other conditions remain constant.

Solution

If the temperature of a gas sample is decreased, the volume decreases as well.

Exercise 8.4.4

What happens to the temperature of a gas if its volume is increased? Assume that all other conditions remain constant.

Answer

The temperature increases.

As with Boyle's law, the relationship between volume and temperature can be expressed in terms of initial and final values of volume and temperature, as follows:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

where V_i and T_i are the initial volume and temperature, and V_f and T_f are the final volume and temperature. This is Charles's law. The restriction on its use is that the pressure of the gas and the amount of gas must remain constant. (Charles's law is sometimes referred to as Gay-Lussac's law, after the scientist who promoted Charles's work.)

Example 8.4.5

A gas sample at 20°C has an initial volume of 20.0 L. What is its volume if the temperature is changed to 60°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Solution

Although the temperatures are given in degrees Celsius, we must convert them to the kelvins before we can use Charles's law. Thus,

$$20°C + 273 = 293\ K = T_i \quad 60°C + 273 = 333\ K = T_f$$

Now we can substitute these values into Charles's law, along with the initial volume of 20.0 L:

$$\frac{20.0\ L}{293\ K} = \frac{V_f}{333\ K}$$

Multiplying the 333 K to the other side of the equation, we see that our temperature units will cancel:

$$\frac{(333\ K)(20.0\ L)}{293\ K} = V_f$$

Solving for the final volume, V_f = 22.7 L. So, as the temperature is increased, the volume increases. This makes sense because volume is directly proportional to the absolute temperature (as long as the pressure and the amount of the remain constant).

Exercise 8.4.5

A gas sample at 35°C has an initial volume of 5.06 L. What is its volume if the temperature is changed to −35°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Answer

3.91 L

Combined Gas Law

Other gas laws can be constructed, but we will focus on only two more. The combined gas law brings Boyle's and Charles's laws together to relate pressure, volume, and temperature changes of a gas sample:

Double subscripts: use braces to clarify

To apply this gas law, the amount of gas should remain constant. As with the other gas laws, the temperature must be expressed in kelvins, and the units on the similar quantities should be the same. Because of the dependence on three quantities at the same time, it is difficult to tell in advance what will happen to one property of a gas sample as two other properties change. The best way to know is to work it out mathematically.

Example 8.4.6

A sample of gas has P_i = 1.50 atm, V_i = 10.5 L, and T_i = 300 K. What is the final volume if P_f = 0.750 atm and T_f = 350 K?

Solution

Using the combined gas law, substitute for five of the quantities:

$$\frac{(1.50\ \text{atm})(10.5\ \text{L})}{300\ \text{K}} = \frac{(0.750\ \text{atm})(\text{V}_\text{f})}{350\ \text{K}}$$

We algebraically rearrange this expression to isolate V_f on one side of the equation:

$$\text{V}_\text{f} = \frac{(1.50\ \text{atm})(10.5\ \text{L})(350\ \text{K})}{(300\ \text{K})(0.750\ \text{atm})} = 24.5\ \text{L}$$

Note how all the units cancel except the unit for volume.

8.4.6 Exercise

A sample of gas has P_i = 0.768 atm, V_i = 10.5 L, and T_i = 300 K. What is the final pressure if V_f = 7.85 L and T_f = 250 K?

Answer

0.856 atm

Example 8.4.7

A balloon containing a sample of gas has a temperature of 22°C and a pressure of 1.09 atm in an airport in Cleveland. The balloon has a volume of 1,070 mL. The balloon is transported by plane to Denver, where the temperature is 11°C and the pressure is 655 torr. What is the new volume of the balloon?

Solution

The first task is to convert all quantities to the proper and consistent units. The temperatures must be expressed in kelvins, and the pressure units are different so one of the quantities must be converted. Let us convert the atmospheres to torr:

$$22°\text{C} + 273 = 295\ \text{K} = T_\text{i}$$

$$11°\text{C} + 273 = 284\ \text{K} = T_\text{f}$$

$$1.09\ \text{atm} \times \frac{760\ \text{torr}}{1\ \text{atm}} = 828\ \text{torr} = \text{P}_\text{i}$$

Now we can substitute the quantities into the combined has law:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})}{295\ \text{K}} = \frac{(655\ \text{torr}) \times \text{V}_\text{f}}{284\ \text{K}}$$

To solve for V_f, we multiply the 284 K in the denominator of the right side into the numerator on the left, and we divide 655 torr in the numerator of the right side into the denominator on the left:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})(284\ \text{K})}{(295\ \text{K})(655\ \text{torr})} = \text{V}_\text{f}$$

Notice that torr and kelvins cancel, as they are found in both the numerator and denominator. The only unit that remains is milliliters, which is a unit of volume. So V_f = 1,300 mL. The overall change is that the volume of the balloon has increased by 230 mL.

8.4.7 Exercise

A balloon used to lift weather instruments into the atmosphere contains gas having a volume of 1,150 L on the ground, where the pressure is 0.977 atm and the temperature is 18°C. Aloft, this gas has a pressure of 6.88 torr and a temperature of −15°C. What is the new volume of the gas?

Answer

110,038 L

The Ideal Gas Law

So far, the gas laws we have used have focused on changing one or more properties of the gas, such as its volume, pressure, or temperature. There is one gas law that relates all the independent properties of a gas under any particular condition, rather than a change in conditions. This gas law is called the ideal gas law. The formula of this law is as follows:

$$PV = nRT$$

In this equation, P is pressure, V is volume, n is amount of moles, and T is temperature. R is called the ideal gas law constant and is a proportionality constant that relates the values of pressure, volume, amount, and temperature of a gas sample. The variables in this equation do not have the subscripts i and f to indicate an initial condition and a final condition. The ideal gas law relates the four independent properties of a gas under *any* conditions.

The value of R depends on what units are used to express the other quantities. If volume is expressed in liters and pressure in atmospheres, then the proper value of R is as follows:

$$\mathrm{R} = 0.08205\ \frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}}$$

This may seem like a strange unit, but that is what is required for the units to work out algebraically.

Example 8.4.8

What is the volume in liters of 1.45 mol of N_2 gas at 298 K and 3.995 atm?

Solution

Using the ideal gas law where P = 3.995 atm, n = 1.45, and T = 298,

$$(3.995\ \mathrm{atm}) \times \mathrm{V} = (1.45\ \mathrm{mol}) \left(0.08205\ \frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}}\right) (298\ \mathrm{K})$$

On the right side, the moles and kelvins cancel. Also, because atmospheres appear in the numerator on both sides of the equation, they also cancel. The only remaining unit is liters, a unit of volume. So

$$3.995 \times V = (1.45)(0.08205)(298)\ \mathrm{L}$$

Dividing both sides of the equation by 3.995 and evaluating, we get V = 8.87 L. Note that the conditions of the gas are not changing. Rather, the ideal gas law allows us to determine what the fourth property of a gas (here, volume) *must* be if three other properties (here, amount, pressure, and temperature) are known.

8.4.8 Exercise

What is the pressure of a sample of CO_2 gas if 0.557 mol is held in a 20.0 L container at 451 K?

Answer

1.03 atm

For convenience, scientists have selected 273 K (0°C) and 1.00 atm pressure as a set of standard conditions for gases. This combination of conditions is called standard temperature and pressure (STP). Under these conditions, 1 mol of any gas has about the same volume. We can use the ideal gas law to determine the volume of 1 mol of gas at STP:

$$(1.00\ \text{atm}) \times \text{V} = (1.00\ \text{mol}) \left(0.08205\ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (273\ \text{K})$$

This volume is 22.4 L. Because this volume is independent of the identity of a gas, the idea that 1 mol of gas has a volume of 22.4 L at STP makes a convenient conversion factor:

$$1\ \text{mol gas} = 22.4\ \text{L (at STP)}$$

Example 8.4.9

Cyclopropane (C_3H_6) is a gas that formerly was used as an anesthetic. How many moles of gas are there in a 100.0 L sample if the gas is at STP?

Solution

We can set up a simple, one-step conversion that relates moles and liters:

$$100.0\ \text{L}\ \text{C}_3\text{H}_6 \times \frac{1\ \text{mol}}{22.4\ \text{L}} = 4.46\ \text{mol}\ \text{C}_3\text{H}_6$$

There are almost 4.5 mol of gas in 100.0 L.

Note: Because of its flammability, cyclopropane is no longer used as an anesthetic gas.

8.4.9 Exercise

Freon is a trade name for a series of fluorine- and chlorine-containing gases that formerly were used in refrigeration systems. What volume does 8.75 mol of Freon have at STP?

Note: Many gases known as Freon are no longer used because their presence in the atmosphere destroys the ozone layer, which protects us from ultraviolet light from the sun.

Answer

196 L

Airbags

Airbags (Figure 8.4.3) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\,\text{NaN}_3(s) \rightarrow 3\,\text{N}_2(g) + 2\,\text{Na}(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.



Figure 8.4.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Dalton's Law of Partial Pressures

The ideal gas equation of state applies to mixtures just as to pure gases. It was in fact with a gas mixture, ordinary air, that Boyle, Gay-Lussac and Charles did their early experiments. The only new concept we need in order to deal with gas mixtures is the *partial pressure*, a concept invented by the famous English chemist John Dalton (1766-1844). Dalton reasoned that the low density and high compressibility of gases indicates that they consist mostly of empty space; from this it follows that when two or more different gases occupy the same volume, they behave entirely independently. The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the *partial pressure* of that gas.

The definition of Dalton's Law of Partial Pressures that address this is:

The total pressure of a gas is the sum of the partial pressures of its components

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3... = \sum_i P_i$$

or, equivalently

$$P_{total} = \frac{RT}{V} \sum_i n_i$$

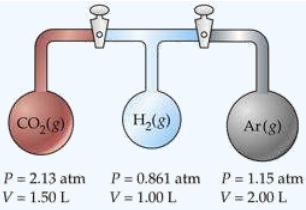
There is also a similar relationship based on *volume fractions*, known as *Amagat's law of partial volumes*. It is exactly analogous to Dalton's law, in that it states that the total volume of a mixture is just the sum of the partial volumes of its components. But there are two important differences: Amagat's law holds only for ideal gases which must all be at the same temperature and pressure. Dalton's law has neither of these restrictions. Although Amagat's law seems intuitively obvious, it sometimes proves useful in chemical engineering applications. We will make no use of it in this course.

Example 8.4.10

Three flasks having different volumes and containing different gases at various pressures are connected by stopcocks as shown. When the stopcocks are opened,

a. What will be the pressure in the system?
b. Which gas will be most abundant in the mixture?

Assume that the temperature is uniform and that the volume of the connecting tubes is negligible.



Solution

The trick here is to note that the total number of moles n_T and the temperature remain unchanged, so we can make use of Boyle's law PV = constant. We will work out the details for CO_2 only, denoted by subscripts *a*.

For CO_2,

$$P_aV_a = (2.13\ atm)(1.50\ L) = 3.20\ L \cdot atm$$

Adding the PV products for each separate container, we obtain

\[\sum_i P_i V_i = 6.36\; L \cdot atm = n_T RT \nonumber \]

We will call this sum P_1V_1. After the stopcocks have been opened and the gases mix, the new conditions are denoted by P_2V_2.

From Boyle's law (8.4.1),

$$P_1V_1 = P_2V_2 = 6.36\ L \cdot atm$$

$$V_2 = \sum_i V_i = 4.50\ L$$

Solving for the final pressure P_2 we obtain (6.36 L-atm)/(4.50 L) = **1.41 atm**.

For part *(b)*, note that the number of moles of each gas is $n = PV/RT$. The mole fraction of any one gas is $X_i = n_i / n_T$. For CO_2, this works out to (3.19/*RT*) / (6.36/*RT*) = 0.501. Because this exceeds 0.5, we know that this is the most abundant gas in the final mixture.

Dalton's law states that in a gas mixture (P_{total}) each gas will exert a pressure independent of the other gases (P_n) and each gas will behave as if it alone occupies the total volume. By extension, the partial pressure of each gas can be calculated by multiplying the total pressure (P_{total}) by the gas percentage (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + ... + P_n$$

or

$$P_n = \frac{n}{P_{Total}}$$

Table 8.4.1: Partial Pressures for the gases in air on a typical day

Gas	Partial Pressure (mm Hg)	Percentage (%)
Nitrogen, (N_2\)	P_{N_2} = 594	78
Oxygen, O_2	P_{O_2} = 160	21
Carbon Dioxide, CO_2	P_{CO_2} = 0.25	0.033
Water Vapor, H_2O	P_{H_2O} = 5.7	0.75
Other trace gases	P_{Other} = 0.05	0.22
Total air	P_{Total} = 760	1

Application of Dalton's Law: Collecting Gases over Water

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a *pneumatic trough*, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.

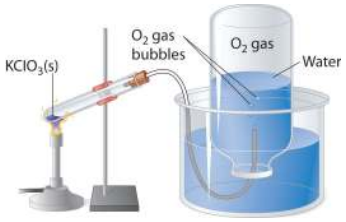


Figure 8.4.1:An Apparatus for Collecting Gases by the Displacement of Water

The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. (An exact calculation would also have to take into account the height of the water column in the inverted tube.) But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H_2O. The partial pressure of H_2O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.

Example 8.4.11

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O_2 produced.

Solution

From Dalton's law,

$$P_{O_2} = P_{total} – P_{H_2O} = 754 – 19.8 = 734\ torr = 0.966\ atm$$

Now use the Ideal Gas Law to convert to moles

$$n = \frac{PV}{RT} = \frac{(0.966\ atm)(0.155\ L)}{(0.082\ Latmmol^{-1}K^{-1})(295\ K)} = 0.00619\ mol$$

Henry’s Law

Henry's law is one of the gas laws formulated by William Henry in 1803. It states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

To explain this law, Henry derived the equation:

$$C = kP_{gas}$$

where

Henry’s Law tells us that the greater the pressure of gas above the surface of a liquid, the higher the concentration of the gas in the liquid. Also, Henry’s law tells us that gases diffuse from areas of high gas concentration to areas of low gas concentration.

Applicability of Henry's Law

- Henry's law only works if the molecules are at equilibrium.
- Henry's law does not work for gases at high pressures (e.g., $N_{2\ (g)}$ at high pressure becomes very soluble and harmful when in the blood supply).
- Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., $HCl_{(g)}$ reacts with water by a dissociation reaction to generate H_3O^+ and Cl^- ions).

Application of Henry's Law: Scuba diving

Our respiratory systems are designed to maintain the proper oxygen concentration in the blood when the partial pressure of O_2 is 0.21 atm, its normal sea-level value. Below the water surface, the pressure increases by 1 atm for each 10.3 m increase in depth; thus a scuba diver at 10.3 m experiences a total of 2 atm pressure pressing on the body. In order to prevent the lungs from collapsing, the air the diver breathes should also be at about the same pressure.

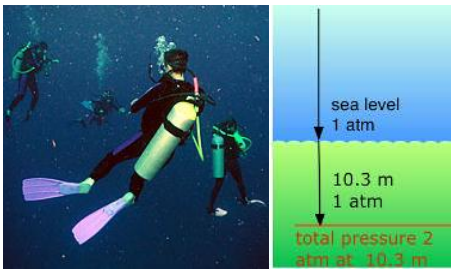


Figure 8.4.2: Scuba Diving actively takes into account both Henry's and Dalton's Laws

But at a total pressure of 2 atm, the partial pressure of O_2 in ordinary air would be 0.42 atm; at a depth of 100 ft (about 30 m), the O_2 pressure of 0.8 atm would be far too high for health. For this reason, the air mixture in the pressurized tanks that scuba divers wear must contain a smaller fraction of O_2. This can be achieved most simply by raising the nitrogen content, but high partial pressures of N_2 can also be dangerous, resulting in a condition known as nitrogen narcosis. The preferred diluting agent for sustained deep diving is helium, which has very little tendency to dissolve in the blood even at high pressures.

Career Focus: Respiratory Therapist

Certain diseases—such as emphysema, lung cancer, and severe asthma—primarily affect the lungs. Respiratory therapists help patients with breathing-related problems. They can evaluate, help diagnose, and treat breathing disorders and even help provide emergency assistance in acute illness where breathing is compromised.

Most respiratory therapists must complete at least two years of college and earn an associate's degree, although therapists can assume more responsibility if they have a college degree. Therapists must also pass state or national certification exams. Once certified, respiratory therapists can work in hospitals, doctor's offices, nursing homes, or patient's homes. Therapists work with equipment such as oxygen tanks and respirators, may sometimes dispense medication to aid in breathing, perform tests, and educate patients in breathing exercises and other therapy.

Because respiratory therapists work directly with patients, the ability to work well with others is a must for this career. It is an important job because it deals with one of the most crucial functions of the body.

Key Takeaway

- The physical properties of gases are predictable using mathematical formulas known as gas laws.
- C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- k is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas (often in units of Atm)

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8.E: Solids, Liquids, and Gases (Exercises)

8.1: Intermolecular Interactions

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.

Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.
2. List the three common phases in the order they exist from lowest energy to highest energy.
3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.
4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.
5. What type of intermolecular interaction is predominate in each substance?
    a. water (H_2O)
    b. sodium sulfate (Na_2SO_4)
    c. decane ($C_{10}H_{22}$)
6. What type of intermolecular interaction is predominate in each substance?
    a. diamond (C, crystal)
    b. helium (He)
    c. ammonia (NH_3)
7. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.
8. Sulfur dioxide (SO_2) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO_2 molecule?
9. What are some of the physical properties of substances that experience covalent network bonding?
10. What are some of the physical properties of substances that experience only dispersion forces?

Answers

1. solid, liquid, and gas

2. solid, liquid, and gas

3. London forces, hydrogen bonding, and ionic interactions

4. dispersion, dipole-dipole, network covalent

5. a. hydrogen bonding
    b. ionic interactions
    c. dispersion forces

6. a. network covalent

b. dispersion
c. hydrogen bonding

7. The two covalent bonds are oriented in such a way that their dipoles cancel out.

8. SO_2 is not a linear molecule. It has a bent or V-shape.

9. very hard, high melting point

10. very soft, very low melting point

8.2: Solids and Liquids

Concept Review Exercise

1. How do the strengths of intermolecular interactions in solids and liquids differ?

Answer

1. Solids have stronger intermolecular interactions than liquids do.

Exercises

1. What are the general properties of solids?
2. What are the general properties of liquids
3. What are the general properties of gases?
4. What phase or phases have a definite volume? What phase or phases do not have a definite volume?
5. Name a common substance that forms a crystal in its solid state.
6. Name a common substance that forms an amorphous solid in its solid state.
7. Are substances with strong intermolecular interactions likely to be solids at higher or lower temperatures? Explain.
8. Are substances with weak intermolecular interactions likely to be liquids at higher or lower temperatures? Explain.
9. State two similarities between the solid and liquid states.
10. State two differences between the solid and liquid states.
11. If individual particles are moving around with respect to each other, a substance may be in either the _____ or _____ state but probably not in the _____ state.
12. If individual particles are in contact with each other, a substance may be in either the _____ or _____ state but probably not in the _____ state.

Answers

1. hard, specific volume and shape, high density, cannot be compressed

2. fixed volume, no definite shape, high density, individual molecules touch each other but in a random way

3. variable volume and shape, low density, compressible

4. solid and liquid have definite volume; gas has no definite volume

5. sodium chloride (answers will vary)

6. glass

7. At higher temperatures, their intermolecular interactions are strong enough to hold the particles in place.

8. Substances with weak intermolecular interactions are likely to be liquids at lower temperatures. Their attractive forces are more easily broken hence they melt more readily.

9. high density; definite volume

10. Solids have definite shape while liquids don't. In solids, molecules occupy fixed positions in a pattern, while in liquids, the molecules are moving in a random arrangement.

11. liquid; gas; solid

12. solid; liquid; gas

8.3: Gases and Pressure

Concept Review Exercise

1. What is pressure, and what units do we use to express it?

Answer

1. Pressure is the force per unit area; its units can be pascals, torr, millimeters of mercury, or atmospheres.

Exercises

1. What is the kinetic theory of gases?
2. According to the kinetic theory of gases, the individual gas particles are (always, frequently, never) moving.
3. Why does a gas exert pressure?
4. Why does the kinetic theory of gases allow us to presume that all gases will show similar behavior?
5. Arrange the following pressure quantities in order from smallest to largest: 1 mmHg, 1 Pa, and 1 atm.
6. Which unit of pressure is larger—the torr or the atmosphere?
7. How many torr are there in 1.56 atm?
8. Convert 760 torr into pascals.
9. Blood pressures are expressed in millimeters of mercury. What would be the blood pressure in atmospheres if a patient’s systolic blood pressure is 120 mmHg and the diastolic blood pressure is 82 mmHg? (In medicine, such a blood pressure would be reported as “120/82,” spoken as “one hundred twenty over eighty-two.”)
10. In weather forecasting, barometric pressure is expressed in inches of mercury (in. Hg), where there are exactly 25.4 mmHg in every 1 in. Hg. What is the barometric pressure in millimeters of mercury if the barometric pressure is reported as 30.21 in. Hg?

Answers

1. Gases are composed of tiny particles that are separated by large distances. Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container. The velocity of gas particles is related to the temperature of a gas. Gas particles do not experience any force of attraction or repulsion with each other.

2. always

3. A gas exerts pressure as its particles rebound off the walls of its container.

4. Because the molecules are far apart and don't have attractive forces between them

5. 1 Pa, 1 mmHg, and 1 atm

6. atm

7. 1,190 torr

8. 98,700 Pa

9. 0.158 atm; 0.108 atm

10. 767.3 mm Hg

8.4: Gas Laws

Concept Review Exercises

1. What properties do the gas laws help us predict?
2. What makes the ideal gas law different from the other gas laws?

Answers

1. Gas laws relate four properties: pressure, volume, temperature, and number of moles.
2. The ideal gas law does not require that the properties of a gas change.

Exercises

1. What conditions of a gas sample should remain constant for Boyle's law to be used?
2. What conditions of a gas sample should remain constant for Charles's law to be used?
3. Does the identity of a gas matter when using Boyle's law? Why or why not?
4. Does the identity of a gas matter when using Charles's law? Why or why not?
5. A sample of nitrogen gas is confined to a balloon that has a volume of 1.88 L and a pressure of 1.334 atm. What will be the volume of the balloon if the pressure is changed to 0.662 atm? Assume that the temperature and the amount of the gas remain constant.
6. A sample of helium gas in a piston has a volume of 86.4 mL under a pressure of 447 torr. What will be the volume of the helium if the pressure on the piston is increased to 1,240 torr? Assume that the temperature and the amount of the gas remain constant.
7. If a gas has an initial pressure of 24,650 Pa and an initial volume of 376 mL, what is the final volume if the pressure of the gas is changed to 775 torr? Assume that the amount and the temperature of the gas remain constant.
8. A gas sample has an initial volume of 0.9550 L and an initial pressure of 564.5 torr. What would the final pressure of the gas be if the volume is changed to 587.0 mL? Assume that the amount and the temperature of the gas remain constant.
9. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is 18°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and amount of the gas remain constant.
10. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is −10°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and the amount of the gas remain constant.
11. An air/gas vapor mix in an automobile cylinder has an initial temperature of 450 K and a volume of 12.7 cm^3. The gas mix is heated to 565°C. If pressure and amount are held constant, what is the final volume of the gas in cubic centimeters?
12. Given the following conditions for a gas: V_i = 0.665 L, T_i = 23.6°C, V_f = 1.034 L. What is T_f in degrees Celsius and kelvins?
13. Assuming the amount remains the same, what must be the final volume of a gas that has an initial volume of 387 mL, an initial pressure of 456 torr, an initial temperature of 65.0°C, a final pressure of 1.00 atm, and a final temperature of 300 K?
14. When the nozzle of a spray can is depressed, 0.15 mL of gas expands to 0.44 mL, and its pressure drops from 788 torr to 1.00 atm. If the initial temperature of the gas is 22.0°C, what is the final temperature of the gas?
15. Use the ideal gas law to show that 1 mol of a gas at STP has a volume of about 22.4 L.
16. Use a standard conversion factor to determine a value of the ideal gas law constant *R* that has units of L•torr/mol•K.
17. How many moles of gas are there in a 27.6 L sample at 298 K and a pressure of 1.44 atm?
18. How many moles of gas are there in a 0.066 L sample at 298 K and a pressure of 0.154 atm?

19. A 0.334 mol sample of carbon dioxide gas is confined to a volume of 20.0 L and has a pressure of 0.555 atm. What is the temperature of the carbon dioxide in kelvins and degrees Celsius?

20. What must *V* be for a gas sample if *n* = 4.55 mol, *P* = 7.32 atm, and *T* = 285 K?

21. What is the pressure of 0.0456 mol of Ne gas contained in a 7.50 L volume at 29°C?

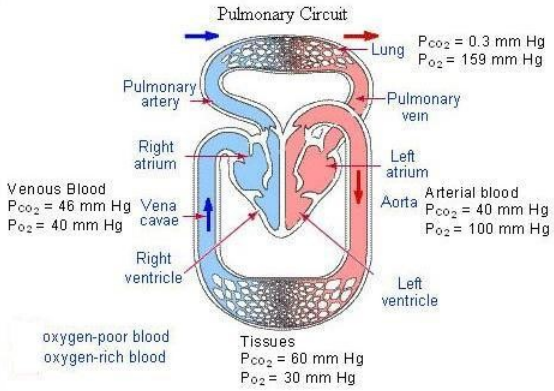
22. What is the pressure of 1.00 mol of Ar gas that has a volume of 843.0 mL and a temperature of −86.0°C?

23. A mixture of the gases N_2, O_2, and Ar has a total pressure of 760 mm Hg. If the partial pressure of N_2 is 220 mm Hg and of O_2 is 470 mm Hg, What is the partial pressure of Ar?

24. What percent of the gas above is Ar?

25. Apply Henry's Law to the diagram below to explain:

why oxygen diffuses from the alveoli of the lungs into the blood and from the blood into the tissues of the body. why carbon dioxide diffuses from the tissues into the blood and from the blood into the alveoli and then finally out into the atmosphere.



Answers

1. temperature and amount of the gas

2. pressure and amount of the gas
3. The identity does not matter because the variables of Boyle's law do not identify the gas.
4. The identity does not matter because the variables of Charles law do not identify the gas.
5. 3.79 L

6. 31.1 mL

7. 92.1 mL

8. 918.4 torr

9. 1.07 L

10. 1.18 L

11. 23.7 cm^3

12. 461 K; 188^0C

13. 206 mL

14. 835 K; 562^0C

15. The ideal gas law confirms that 22.4 L equals 1 mol.

16. $\frac{760\ torr}{1\ atm}$

17. 1.63 mol

18. 4.2×10^{-4} mol

19. 405 K; 132°C

20. 14.5 L

21. 0.151 atm

22. 18.2 atm

23. 70 mm Hg

24. 9.2%

25. Gases diffuse from high concentration to low concentration (Henry's Law). The partial pressure of **oxygen** is high in the **alveoli** and low in the **blood** of the pulmonary capillaries. As a result, **oxygen diffuses** across the respiratory membrane from the **alveoli** into the **blood**. It's also higher partial pressure in the blood than in the tissues, hence it transfers to the tissues. On the other hand, carbon dioxide **diffuses** from the tissues (highest CO_2 partial pressure) and across the respiratory membrane from the **blood** into the **alveoli** and out **to the atmosphere.**

Additional Exercises

1. How many grams of oxygen gas are needed to fill a 25.0 L container at 0.966 atm and 22°C?
2. A breath of air is about 1.00 L in volume. If the pressure is 1.00 atm and the temperature is 37°C, what mass of air is contained in each breath? Use an average molar mass of 28.8 g/mol for air.
3. The balanced chemical equation for the combustion of propane is as follows:

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(\ell)} \tag{8.E.1}$$

   a. If 100.0 g of propane are combusted, how many moles of oxygen gas are necessary for the reaction to occur?
   b. At STP, how many liters of oxygen gas would that be?

4. The equation for the formation of ammonia gas (NH_3) is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \tag{8.E.2}$$

   At 500°C and 1.00 atm, 10.0 L of N_2 gas are reacted to make ammonia.

   a. If the pressures and temperatures of H_2 and NH_3 were the same as those of N_2, what volume of H_2 would be needed to react with N_2, and what volume of NH_3 gas would be produced?
   b. Compare your answers to the balanced chemical equation. Can you devise a “shortcut” method to answer Exercise 4a?

5. At 20°C, 1 g of liquid H_2O has a volume of 1.002 mL. What volume will 1 g of water vapor occupy at 20°C if its pressure is 17.54 mmHg? By what factor has the water expanded in going from the liquid phase to the gas phase?
6. At 100°C, 1 g of liquid H_2O has a volume of 1.043 mL. What volume will 1 g of steam occupy at 100°C if its pressure is 760.0 mmHg? By what factor has the water expanded in going from the liquid phase to the gas phase?
7. Predict whether NaCl or NaI will have the higher melting point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
8. Predict whether CH_4 or CH_3OH will have the lower boiling point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
9. A standard automobile tire has a volume of about 3.2 ft^3 (where 1 ft^3 equals 28.32 L). Tires are typically inflated to an absolute pressure of 45.0 pounds per square inch (psi), where 1 atm equals 14.7 psi. Using this information with the ideal gas law, determine the number of moles of air needed to fill a tire if the air temperature is 18.0°C.
10. Another gas law, Amontons’s law, relates pressure and temperature under conditions of constant amount and volume:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

    If an automobile tire (see Exercise 9) is inflated to 45.0 psi at 18.0°C, what will be its pressure if the operating temperature (i.e., the temperature the tire reaches when the automobile is on the road) is 45.0°C? Assume that the volume and the amount of the

gas remain constant.

Answers

1. 31.9 g

2. 1.13 g

3.

   a. 11.4 mol
   b. 255 L

4.

   a. 30.0 L H_2 and 20.0 L NH_3

   b. the mole ratio in the balanced equation is the same as the volume ratio.

$$10.0\ \text{L}\ \text{N}_2 \times \frac{3\ \text{L}\ \text{H}_2}{1\ \text{L}\ \text{N}_2} = 30.0\ \text{L}\ \text{H}_2$$

$$10.0\ \text{L}\ \text{N}_2 \times \frac{2\ \text{L}\ \text{NH}_3}{1\ \text{L}\ \text{N}_2} = 20.0\ \text{L}\ \text{NH}_3$$

5. 57.75 L; an expansion of 57,600 times

6. 1.698 L; an expansion of 1,628 times

7. NaCl; with smaller anions, NaCl likely experiences stronger ionic bonding.

8. CH_4 will have the lower boiling point because its intermolecular force (London dispersion force only) is weaker than those in CH_3OH. Aside from London dispersion, CH_3OH has dipole-dipole and hydrogen bonding.

9. 11.6 mol

10. 49.2 psi

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8.S: Solids, Liquids, and Gases (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.

A **phase** is a certain form of matter that has the same physical properties throughout. Three phases are common: the solid, the liquid, and the gas phase. What determines the phase of a substance? Generally, the strength of the **intermolecular interactions** determines whether a substance is a solid, liquid, or gas under any particular conditions. **Covalent network bonding** is a very strong form of intermolecular interaction. Diamond is one example of a substance that has this intermolecular interaction. **Ionic interactions**, the forces of attraction due to oppositely charged ions, are also relatively strong. Covalent bonds are another type of interaction within molecules, but if the bonds are **polar covalent bonds**, then the unequal sharing of electrons can cause charge imbalances within molecules that cause interactions between molecules. These molecules are described as **polar**, and these interactions are called **dipole-dipole interactions**. A certain rather strong type of dipole-dipole interaction, involving a hydrogen atom, is called **hydrogen bonding**. On the other hand, equal sharing of electrons forms **nonpolar covalent bonds**, and the interactions between different molecules is less because the molecules are nonpolar. All substances have very weak **dispersion forces** (also called **London forces**) caused by the movement of electrons within the bonds themselves.

In the solid phase, intermolecular interactions are so strong that they hold the individual atoms or molecules in place. In many solids, the regular three-dimensional arrangement of particles makes a **crystal**. In other solids, the irregular arrangement of particles makes an **amorphous** solid. In liquids, the intermolecular interactions are strong enough to keep the particles of substance together but not in place. Thus, the particles are free to move over each other but still remain in contact.

In gases, the intermolecular interactions are weak enough that the individual particles are separated from each other in space. The **kinetic theory of gases** is a collection of statements that describe the fundamental behavior of all gases. Among other properties, gases exert a **pressure** on their container. Pressure is measured using units like **pascal**, **bar**, **atmosphere**, or **mmHg** (also called a **torr**).

There are several simple relationships between the variables used to describe a quantity of gas. These relationships are called **gas laws**. **Boyle's law** relates the pressure and volume of a gas, while **Charles's law** relates the volume and absolute temperature of a gas. The **combined gas law** relates the volume, pressure, and absolute temperature of a gas sample. All of these gas laws allow us to understand the changing conditions of a gas. The **ideal gas law** relates the pressure, volume, amount, and absolute temperature of a gas under any conditions. These four variables are related to the **ideal gas law constant**, which is the proportionality constant used to calculate the conditions of a gas. Because the conditions of a gas can change, a set of benchmark conditions called **standard temperature and pressure (STP)** is defined. Standard temperature is 0ºC, and standard pressure is 1.00 atm.

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CHAPTER OVERVIEW

9: 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.

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9.0: 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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9.1: 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 9.1.1 lists some common types of solutions, with examples of each.

Table 9.1.1: 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 9.1.1).



Figure 9.1.1: 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 9.1.1

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 9.1.1

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 9.1.2

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.

9.1.2 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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9.2: 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 9.2.1 lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table 9.2.1 includes the temperature at which the solubility was determined.

Table 9.2.1: 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 9.2.1. 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 9.2.1***:*** 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:

$$\%\ \text{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Example 9.2.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\ \text{m/m} = \frac{36.5\ \text{g}}{355\ \text{g}} \times 100\% = 10.3\%$$

Exercise 9.2.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer

7.90%

For gases and liquids, volumes are relatively easy to measure, so the concentration of a liquid or a gas solution can be expressed as a **volume/volume percent** (% v/v): the volume of a solute divided by the volume of a solution times 100:

$$\%\ \text{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

Again, the units of the solute and the solution must be the same. A hybrid concentration unit, **mass/volume percent** (% m/v), is commonly used for intravenous (IV) fluids (Figure 9.2.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\%\ \text{m/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$$



Figure 9.2.1: 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:

$$\frac{5\ \text{mL alcohol}}{100\ \text{mL solution}} \text{ or } \frac{100\ \text{mL solution}}{5\ \text{mL alcohol}}$$

Use the first conversion factor to convert from a given amount of solution to amount of solute. The second conversion factor is used to convert from a given amount of solute to amount of solution. Given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

Example 9.2.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

Solution

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\%\ \text{v/v} \rightarrow \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}}$$

That is, there are 45 mL of C_2H_5OH for every 100 mL of solution. We can use this fraction as a **conversion factor** to determine the amount of C_2H_5OH in 115 mL of solution:

$$115 \text{ mL solution} \times \frac{45 \text{ mL } C_2H_5OH}{100 \text{ mL solution}} = 51.8 \text{ mL } C_2H_5OH$$

Exercise 9.2.2

What volume of a 12.75% m/v solution of glucose ($C_6H_{12}O_6$) in water is needed to obtain 50.0 g of $C_6H_{12}O_6$?

Answer

$$50.0 \text{ g } C_6H_12O_6 \times \frac{100 \text{ mL solution}}{12.75 \text{ g } C_6H_12O_6} = 392 \text{ mL solution}$$

Example 9.2.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?

Solution

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

$$1 \text{ L} = 1{,}000 \text{ mL}$$

Because this is an exact relationship, it does not affect the significant figures of our result.

$$\%\text{ m/v} = \frac{9.0 \text{ g NaCl}}{1{,}000 \text{ mL solution}} \times 100\% = 0.90\%\text{ m/v}$$

Exercise 9.2.3

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:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1{,}000{,}000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1{,}000{,}000{,}000$$

> *Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).*

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

> *In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.*

Example 9.2.4

If the concentration of cobalt in a human body is 21 ppb, what mass in grams of Co is present in a body having a mass of 70.0 kg?

Solution

A concentration of 21 ppb means "21 g of solute per 1,000,000,000 g of solution." Written as a **conversion factor,** this concentration of Co is as follows:

$$21 \text{ ppb Co} \rightarrow \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}}$$

We can use this as a conversion factor, but first we must convert 70.0 kg to gram units:

$$70.0 \text{ kg} \times \frac{1,000 \text{ g}}{1 \text{ kg}} = 7.00 \times 10^4 \text{ g}$$

Now we determine the amount of Co:

$$7.00 \times 10^4 \text{ g solution} \times \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}} = 0.0015 \text{ g Co}$$

This is only 1.5 mg.

Exercise 9.2.4

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:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

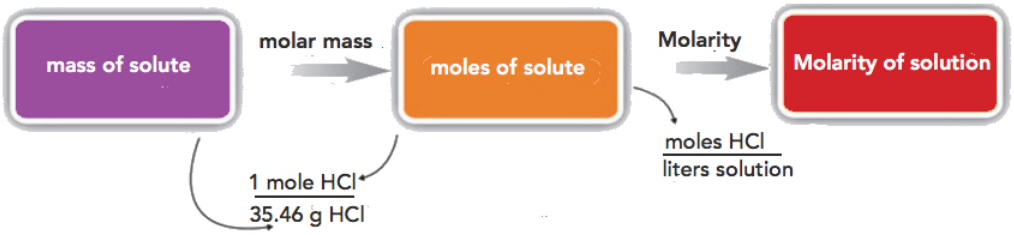
Molarity is abbreviated M (often referred to as "molar"), and the units are often abbreviated as mol/L. It is important to remember that "mol" in this expression refers to moles of solute and that "L" refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

which is read as "three point oh **molar** sodium chloride." Sometimes (aq) is added when the solvent is water, as in "3.0 M NaCl(aq)."

Before a molarity concentration can be calculated, the amount of the **solute must be expressed in moles**, and the **volume of the solution** must be expressed in **liters**.

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?



Step 1: convert the **mass of solute** to **moles** using the **molar mass of HCl (36.46 g/mol):**

$$22.4\ \cancel{g HCl} \times \frac{1\ mol\ HCl}{36.46\ \cancel{g HCl}} = 0.614\ mol\ HCl$$

Step 2: use the **definition of molarity** to determine the concentration:

$$M\ =\ \frac{0.614\ mol\ HCl}{1.56 L\ solution} = 0.394\ MHCl$$

Example 9.2.5

What is the molarity of an aqueous solution of 25.0 g of NaOH in 750 mL?

Solution

Before we substitute these quantities into the definition of molarity, we must convert them to the proper units. The mass of NaOH must be converted to moles of NaOH. The molar mass of NaOH is 40.00 g/mol:

$$25.0\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 0.625\ \text{mol NaOH}$$

Next, we convert the volume units from milliliters to liters:

$$750\ \text{mL} \times \frac{1\ \text{L}}{1,000\ \text{mL}} = 0.750\ \text{L}$$

Now that the quantities are expressed in the proper units, we can substitute them into the definition of molarity:

$$\text{M} = \frac{0.625\ \text{mol NaOH}}{0.750\ \text{L}} = 0.833\ \text{M NaOH}$$

Exercise 9.2.5

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**.

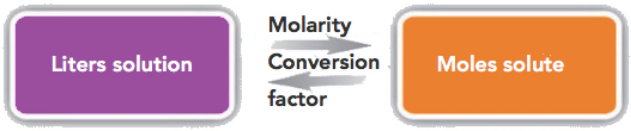
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a **3.0 M solution of sucrose** means that there are three moles of sucrose dissolved in every **liter of solution**. Mathematically, this is stated as follows:

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.

$$0.108 \cancel{L\ solution} \times \frac{3.0\ mol\ sucrose}{1 \cancel{L\ solution}} = 0.32\ mol\ sucrose$$

How many liters of 3.0 M sucrose solution are needed to obtain 4.88 mol of sucrose? In such a conversion, we multiply the given (4.88 moles sucrose) with the second conversion factor. This cancels the moles units and converts it to liters of solution.

$$4.88 \cancel{mol\ sucrose} \times \frac{1\ L\ solution}{3.0 \cancel{mol\ sucrose}} = 1.63\ L\ solution$$

Example 9.2.6

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.

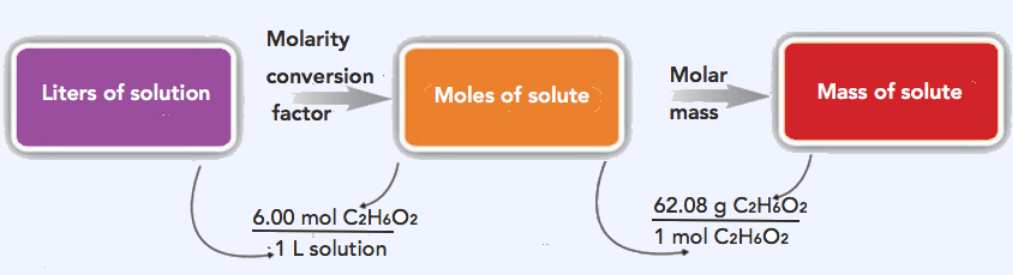
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00 \text{ L solution} \times \frac{6.00 \text{ mol } C_2H_6O_2}{1 \text{ L solution}} = 30.0 \text{ mol } C_2H_6O_2$$

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 9.2.6A

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. $0.0753\ \text{M} = \dfrac{0.450\ \text{mol}\ (CH_3)_2NH}{\text{volume of solution}}$

   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 9.2.6

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:

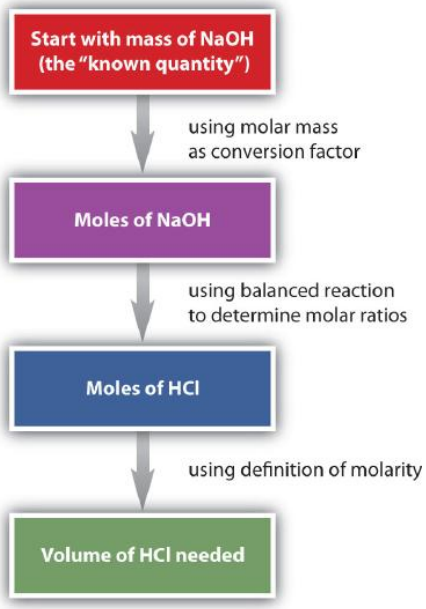


Figure 9.2.2*: Typical approach to solving Molarity problems*

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving.

Example 9.2.7

How many milliliters of a 2.75 M HCl solution are needed to react with 185 g of NaOH? The balanced chemical equation for this reaction is as follows:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Solution

We will follow the flowchart to answer this question. First, we convert the mass of NaOH to moles of NaOH using its molar mass, 40.00 g/mol:

$$185\ \text{g NaOH} \times \frac{1\ \text{mol NaOH}}{40.00\ \text{g NaOH}} = 4.63\ \text{mol NaOH}$$

Using the balanced chemical equation, we see that there is a one-to-one ratio of moles of HCl to moles of NaOH. We use this to determine the number of moles of HCl needed to react with the given amount of NaOH:

$$4.63\ \text{mol NaOH} \times \frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}} = 4.63\ \text{mol HCl}$$

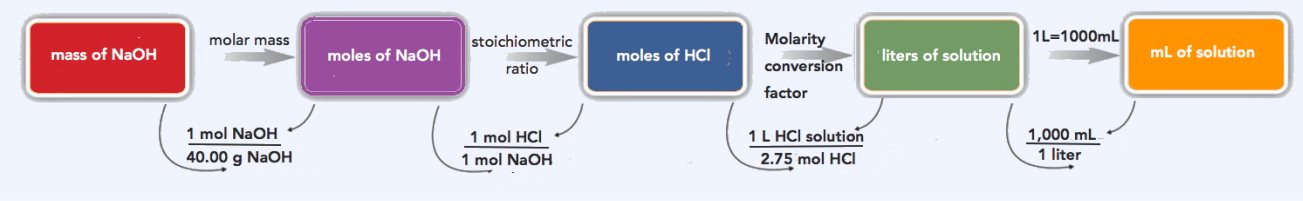
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$2.75\ \text{M HCl} = \frac{4.63\ \text{mol HCl}}{\text{volume of HCl solution}}$$

$$\text{volume of HCl} = \frac{4.63\ \text{mol HCl}}{2.75\ \text{M HCl}} = 1.68\ \text{L} \times \frac{1,000\ \text{mL}}{1\ \text{L}} = 1,680\ \text{mL}$$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

The same multi-step problem can also be worked out in a single line, rather than as separate steps, as follows:



$$185\text{ g NaOH} \times \frac{1\text{ mol NaOH}}{40.00\text{ g NaOH}} \times \frac{1\text{ mol HCl}}{1\text{ mol NaOH}} \times \frac{1\text{ L HCl solution}}{2.75\text{ mol HCl}} \times \frac{1000\text{ mL HCl solution}}{1\text{ L HCl solution}} = 1,680\text{ mL HCl solution}$$

Our final answer (rounded off to three significant figures) is 1,680 mL HCl solution.

? Exercise 9.2.7

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 9.2.3. You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure 9.2.3 indicate that you can start at either end of the chart and, after a series of simple conversions, determine the quantity at the other end.

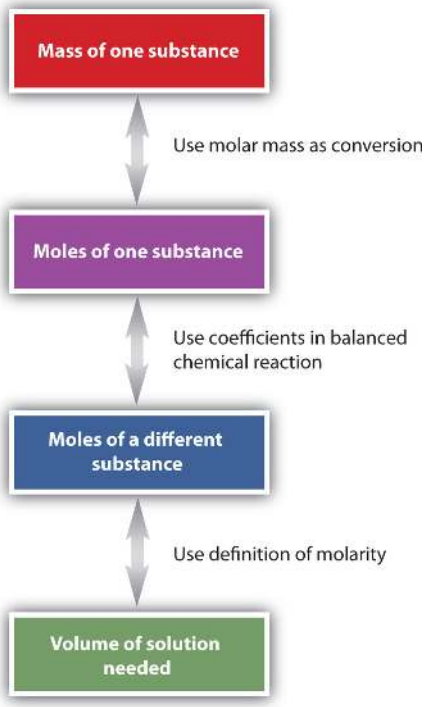


Figure 9.2.3: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table 9.2.2 lists the typical concentrations of some of these solutes.

Table 9.2.2: 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, Section 3.3.)

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).

$$\text{mol}_1 = \text{mol}_2$$

Since the moles of solute in a solution is equal to the molarity multiplied by the liters, we can set those equal.

$$M_1 \times L_1 = M_2 \times L_2$$

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:

$$M_1 \times V_1 = M_2 \times V_2$$

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

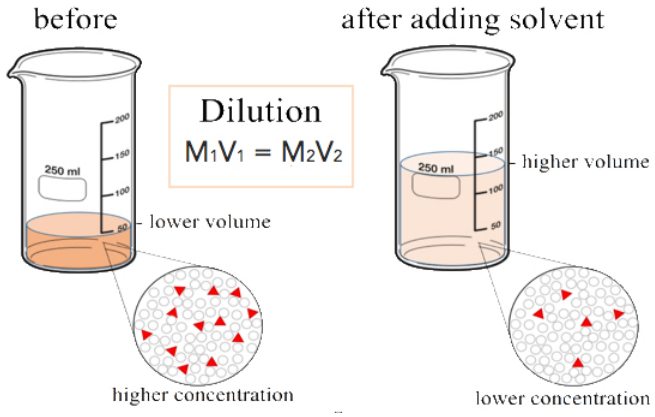


Figure 9.2.1: Figure 9.2.4: Diluting a solution by adding more solvent. Through the dilution process, the volume increases and the concentrations of the solutes decrease. As a consequence, there is more solution in the beaker after dilution, and the color of the solution becomes fainter. The inset shows 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:

$$\text{Molarity}_{\text{initial}} \times \text{volume}_{\text{initial}} = \text{Molarity}_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$\boldsymbol{M_1V_1 = M_2V_2}$$

If we are using percent, the dilution equation is as follows:

$$\%_{\text{initial}} \times \text{volume}_{\text{initial}} = \%_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$\boldsymbol{\%_1V_1 = \%_2V_2}$$

Example 9.2.8

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)$_{\text{initial}}$ = (concentration × volume)$_{\text{final}}$:

$$(0.900\ \text{M} \times 125\ \text{mL}) = (\text{concentration} \times 1{,}125\ \text{mL})$$

We solve by isolating the unknown concentration by itself on one side of the equation. Dividing by 1,125 mL gives

$$\text{concentration} = \frac{0.900\ \text{M} \times 125\ \text{mL}}{1,125\ \text{mL}} = 0.100\ \text{M}$$

as the final concentration.

Exercise 9.2.8

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 9.2.5:*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.

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9.3: 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 9.3.1. When the solvent is water, the word **hydration**, rather than solvation, is used.

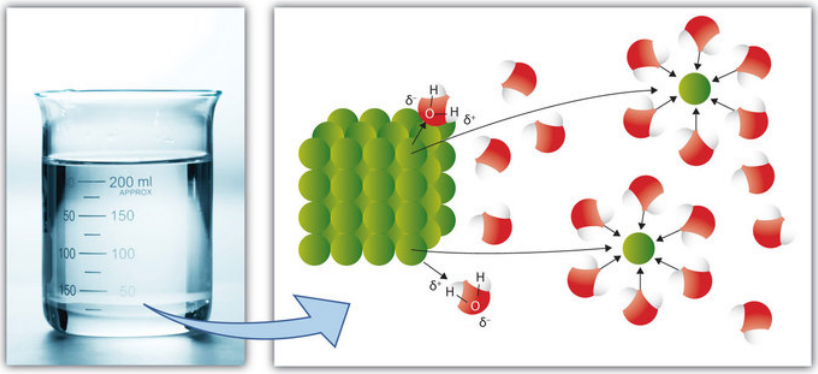


Figure 9.3.1: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

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 9.3.1).

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 9.3.1

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 9.3.1

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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9.4: Properties of Solutions

Learning Objectives

- To describe how the properties of solutions differ from those of pure solvents.

Solutions are likely to have properties similar to those of their major component—usually the solvent. However, some solution properties differ significantly from those of the solvent. Here, we will focus on liquid solutions that have a solid solute, but many of the effects we will discuss in this section are applicable to all solutions.

Colligative Properties

Solutes affect some properties of solutions that depend only on the concentration of the dissolved particles. These properties are called **colligative properties**. Four important colligative properties that we will examine here are vapor pressure depression, boiling point elevation, freezing point depression, and osmotic pressure.

Molecular compounds separate into individual molecules when they are dissolved, so for every 1 mol of molecules dissolved, we get 1 mol of particles. In contrast, **ionic** compounds separate into their constituent ions when they dissolve, so 1 mol of an ionic compound will produce more than 1 mol of dissolved particles. For example, **every mole of NaCl** that dissolves yields **1 mol of Na^+ ions** and **1 mol of Cl^- ions**, for a **total of 2 mol** of particles in solution. Thus, the effect on a solution's properties by dissolving NaCl may be twice as large as the effect of dissolving the same amount of moles of glucose ($C_6H_{12}O_6$).

Vapor Pressure Depression

All liquids evaporate. In fact, given enough volume, a liquid will turn completely into a vapor. If enough volume is not present, a liquid will evaporate only to the point where the rate of evaporation equals the rate of vapor condensing back into a liquid. The pressure of the vapor at this point is called the **vapor pressure** of the liquid.

The presence of a dissolved solid lowers the characteristic vapor pressure of a liquid so that it evaporates more slowly. (The exceptions to this statement are if the solute itself is a liquid or a gas, in which case the solute will also contribute something to the evaporation process. We will not discuss such solutions here.) This property is called vapor pressure depression and is depicted in Figure 9.4.1.

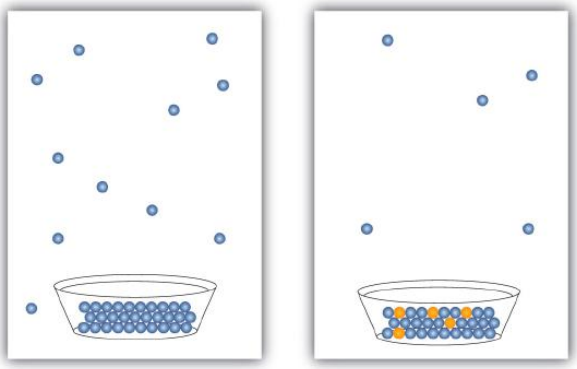


Figure 9.4.1: Vapor Pressure Depression. The presence of solute particles blocks some of the ability for liquid particles to evaporate. Thus, solutions of solid solutes typically have a lower vapor pressure than the pure solvent.

Boiling Point and Freezing Point Effects

A related property of solutions is that their boiling points are higher than the boiling point of the pure solvent. Because the presence of solute particles decreases the vapor pressure of the liquid solvent, a higher temperature is needed to reach the boiling point. This phenomenon is called boiling point elevation. **For every mole of particles dissolved in a liter of water, the boiling point of water increases by about 0.5°C.** The addition of one mole of sucrose (molecular compound) in one liter of water will raise the boiling point from 100^0C to 100.5^0C but the addition of one mole of NaCl in one liter of water will raise the boiling point by 2 x 0.5^0C = 1^0C. Furthermore, the addition of one mole of $CaCl_2$ in one liter of water will raise the boiling point by 3 x 0.5^0C = 1.5^0C.

Some people argue that putting a pinch or two of salt in water used to cook spaghetti or other pasta makes a solution that has a higher boiling point, so the pasta cooks faster. In actuality, the amount of solute is so small that the boiling point of the water is practically unchanged.

The presence of solute particles has the opposite effect on the freezing point of a solution. When a solution freezes, only the solvent particles come together to form a solid phase, and the presence of solute particles interferes with that process. Therefore, for the liquid solvent to freeze, more energy must be removed from the solution, which lowers the temperature. Thus, solutions have lower freezing points than pure solvents do. This phenomenon is called freezing point depression. **For every mole of particles in a liter of water, the freezing point decreases by about 1.9°C.**

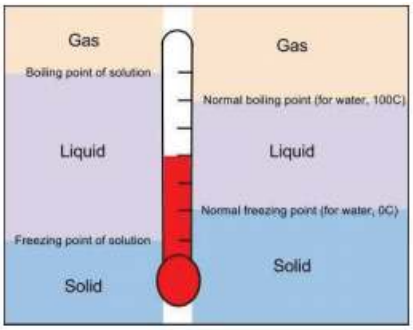


Figure 9.4.2: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

Both boiling point elevation and freezing point depression have practical uses. For example, solutions of water and ethylene glycol ($C_2H_6O_2$) are used as coolants in automobile engines because the boiling point of such a solution is greater than 100°C, the normal boiling point of water. In winter, salts like NaCl and $CaCl_2$ are sprinkled on the ground to melt ice or keep ice from forming on roads and sidewalks (Figure 9.4.2). This is because the solution made by dissolving sodium chloride or calcium chloride in water has a lower freezing point than pure water, so the formation of ice is inhibited.



Figure 9.4.2: Effect of Freezing Point Depression. The salt sprinkled on this sidewalk makes the water on the sidewalk have a lower freezing point than pure water, so it does not freeze as easily. This makes walking on the sidewalk less hazardous in winter. © Thinkstock

Example 9.4.1

Which solution's freezing point deviates more from that of pure water—a 1 M solution of NaCl or a 1 M solution of $CaCl_2$?

Solution

Colligative properties depend on the number of dissolved particles, so the solution with the greater number of particles in solution will show the greatest deviation. When NaCl dissolves, it separates into two ions, Na^+ and Cl^-. But when $CaCl_2$ dissolves, it separates into three ions—one Ca^{2+} ion and two Cl^- ions. Thus, mole for mole, $CaCl_2$ will have 50% more impact on freezing point depression than NaCl.

? Exercise 9.4.1

Which solution's boiling point deviates more from that of pure water—a 1 M solution of $CaCl_2$ or a 1 M solution of $MgSO_4$?

Answer

$CaCl_2$

✓ Example 9.4.2

Estimate the boiling point of 0.2 M $CaCl_2$ solution.

Solution

The boiling point increases 0.5^0C for every mole of solute per liter of water. For this estimation, let's assume that 1 liter of solution is roughly the same volume as 1 liter of water. A 0.2 M $CaCl_2$ solution contains 0.2 moles of $CaCl_2$ solution formula units per liter of solution. Each $CaCl_2$ unit separates into three ions.

$$0.2 \text{ mol } CaCl_2 \times \frac{3 \text{ mol ions}}{1 \text{ mol } CaCl_2} \times \frac{0.5 \text{ deg C}}{1 \text{ mol ion}} = 0.3 \text{ deg C}$$

The normal boiling point of water is 100^0C, so the boiling point of the solution is raised to 100.3^0C.

9.4.2Exercise

Estimate the freezing point of 0.3 M $CaCl_2$ solution.

Answer

minus 1.7^0C

Osmotic Pressure

The last colligative property of solutions we will consider is a very important one for biological systems. It involves **osmosis**, the process by which solvent molecules can pass through certain membranes but solute particles cannot. When two solutions of different concentration are present on either side of these membranes (called *semipermeable membranes*), there is a tendency for solvent molecules to move from the more dilute solution to the more concentrated solution until the concentrations of the two solutions are equal. This tendency is called **osmotic pressure**. External pressure can be exerted on a solution to counter the flow of solvent; the pressure required to halt the osmosis of a solvent is equal to the osmotic pressure of the solution.

Osmolarity (osmol) is a way of reporting the total number of particles in a solution to determine osmotic pressure. It is defined as the molarity of a solute times the number of particles a formula unit of the solute makes when it dissolves (represented by i):

$$osmol = M \times i \tag{9.4.1}$$

If more than one solute is present in a solution, the individual osmolarities are additive to get the total osmolarity of the solution. Solutions that have the same osmolarity have the same osmotic pressure. If solutions of differing osmolarities are present on opposite sides of a semipermeable membrane, solvent will transfer from the lower-osmolarity solution to the higher-osmolarity solution. Counterpressure exerted on the high-osmolarity solution will reduce or halt the solvent transfer. An even higher pressure can be exerted to force solvent from the high-osmolarity solution to the low-osmolarity solution, a process called *reverse osmosis*. Reverse osmosis is used to make potable water from saltwater where sources of fresh water are scarce.

✓ Example 9.4.3

A 0.50 M NaCl aqueous solution and a 0.30 M $Ca(NO_3)_2$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Solution

The solvent will flow into the solution of higher osmolarity. The NaCl solute separates into two ions—Na^+ and Cl^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol (NaCl)} = 0.50\ \text{M} \times 2 = 1.0\ \text{osmol}$$

The $Ca(NO_3)_2$ solute separates into three ions—one Ca^{2+} and two NO_3^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol } [Ca(NO_3)_2] = 0.30\ \text{M} \times 3 = 0.90\ \text{osmol}$$

The osmolarity of the $Ca(NO_3)_2$ solution is lower than that of the NaCl solution, so water will transfer through the membrane from the $Ca(NO_3)_2$ solution to the NaCl solution.

? Exercise 9.4.3

A 1.5 M $C_6H_{12}O_6$ aqueous solution and a 0.40 M $Al(NO_3)_3$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Answer

osmol $C_6H_{12}O_6$ = 1.5; osmol $Al(NO_3)_3$ = 1.6

The solvent flows from $C_6H_{12}O_6$ solution (lower osmolarity) to $Al(NO_3)_3$ solution (higher osmolarity).

To Your Health: Dialysis

The main function of the kidneys is to filter the blood to remove wastes and extra water, which are then expelled from the body as urine. Some diseases rob the kidneys of their ability to perform this function, causing a buildup of waste materials in the bloodstream. If a kidney transplant is not available or desirable, a procedure called dialysis can be used to remove waste materials and excess water from the blood.

In one form of dialysis, called *hemodialysis*, a patient's blood is passed though a length of tubing that travels through an *artificial kidney machine* (also called a *dialysis machine*). A section of tubing composed of a semipermeable membrane is immersed in a solution of sterile water, glucose, amino acids, and certain electrolytes. The osmotic pressure of the blood forces waste molecules and excess water through the membrane into the sterile solution. Red and white blood cells are too large to pass through the membrane, so they remain in the blood. After being cleansed in this way, the blood is returned to the body.



Figure 9.4.3: A patient undergoing hemodialysis depends on osmosis to cleanse the blood of waste products that the kidneys are incapable of removing due to disease. from Wikipedia.

Dialysis is a continuous process, as the osmosis of waste materials and excess water takes time. Typically, 5–10 lb of waste-containing fluid is removed in each dialysis session, which can last 2–8 hours and must be performed several times a week. Although some patients have been on dialysis for 30 or more years, dialysis is always a temporary solution because waste materials are constantly building up in the bloodstream. A more permanent solution is a kidney transplant.

Cell walls are semipermeable membranes, so the osmotic pressures of the body's fluids have important biological consequences. If solutions of different osmolarity exist on either side of the cells, solvent (water) may pass into or out of the cells, sometimes with disastrous results. Consider what happens if red blood cells are placed in a *hypotonic* solution, meaning a solution of lower

osmolarity than the liquid inside the cells. The cells swell up as water enters them, disrupting cellular activity and eventually causing the cells to burst. This process is called *hemolysis*. If red blood cells are placed in a *hypertonic* solution, meaning one having a higher osmolarity than exists inside the cells, water leaves the cells to dilute the external solution, and the red blood cells shrivel and die. This process is called *crenation*. Only if red blood cells are placed in *isotonic* solutions that have the same osmolarity as exists inside the cells are they unaffected by negative effects of osmotic pressure. **Glucose solutions of about 0.31 M, or sodium chloride solutions of about 0.16 M, are isotonic with blood plasma.**

> The concentration of an isotonic sodium chloride (NaCl) solution is only half that of an isotonic glucose ($C_6H_{12}O_6$) solution because NaCl produces two ions when a formula unit dissolves, while molecular $C_6H_{12}O_6$ produces only one particle when a formula unit dissolves. The osmolarities are therefore the same even though the concentrations of the two solutions are different.

Osmotic pressure explains why you should not drink seawater if you are abandoned in a life raft in the middle of the ocean. Its osmolarity is about three times higher than most bodily fluids. You would actually become thirstier as water from your cells was drawn out to dilute the salty ocean water you ingested. Our bodies do a better job coping with hypotonic solutions than with hypertonic ones. The excess water is collected by our kidneys and excreted.

Osmotic pressure effects are used in the food industry to make pickles from cucumbers and other vegetables and in brining meat to make corned beef. It is also a factor in the mechanism of getting water from the roots to the tops of trees!

Career Focus: Perfusionist

A perfusionist is a medical technician trained to assist during any medical procedure in which a patient's circulatory or breathing functions require support. The use of perfusionists has grown rapidly since the advent of open-heart surgery in 1953.

Most perfusionists work in operating rooms, where their main responsibility is to operate heart-lung machines. During many heart surgeries, the heart itself must be stopped. In these situations, a heart-lung machine keeps the patient alive by aerating the blood with oxygen and removing carbon dioxide. The perfusionist monitors both the machine and the status of the blood, notifying the surgeon and the anesthetist of any concerns and taking corrective action if the status of the blood becomes abnormal.

Despite the narrow parameters of their specialty, perfusionists must be highly trained. Certified perfusion education programs require a student to learn anatomy, physiology, pathology, chemistry, pharmacology, math, and physics. A college degree is usually required. Some perfusionists work with other external artificial organs, such as hemodialysis machines and artificial livers.

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9.5: 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.

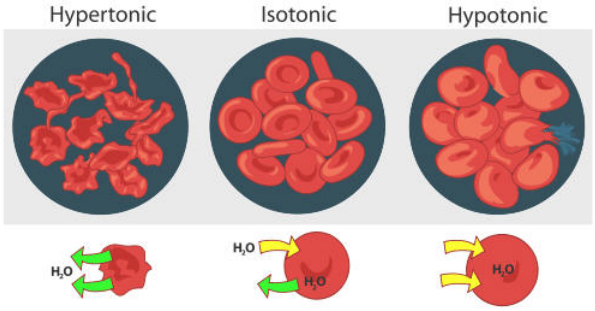


Figure 9.7.1: Red blood cells in hypertonic, isotonic, and hypotonic solutions.

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.

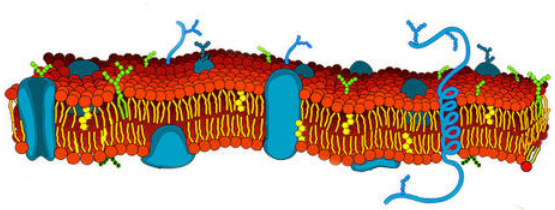


Figure 9.7.2: Plasma membranes are primarily made up of phospholipids (orange). The hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails are shown. The phospholipids form a bilayer (two layers). The middle of the bilayer is an area without water. There can be water on either side 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

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).

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9.E: Solutions (Exercises)

9.1: Solutions

Concept Review Exercises

1. What causes a solution to form?
2. How does the phrase *like dissolves like* relate to solutions?

Answers

1. Solutions form because a solute and a solvent have similar intermolecular interactions.
2. It means that substances with similar intermolecular interactions will dissolve in each other.

Exercises

1. Define *solution*.
2. Give several examples of solutions.
3. What is the difference between a solvent and a solute?
4. Can a solution have more than one solute in it? Can you give an example?
5. Does a solution have to be a liquid? Give several examples to support your answer.
6. Give at least two examples of solutions found in the human body.
7. Which substances will probably be soluble in water, a very polar solvent?
   a. sodium nitrate ($NaNO_3$)
   b. hexane (C_6H_{14})
   c. isopropyl alcohol [$(CH_3)_2CHOH$]
   d. benzene (C_6H_6)
8. Which substances will probably be soluble in toluene ($C_6H_5CH_3$), a nonpolar solvent?
   a. sodium nitrate ($NaNO_3$)
   b. hexane (C_6H_{14})
   c. isopropyl alcohol [$(CH_3)_2CHOH$]
   d. benzene (C_6H_6)
9. The solubility of alcohols in water varies with the length of carbon chain. For example, ethanol (CH_3CH_2OH) is soluble in water in any ratio, while only 0.0008 mL of heptanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$) will dissolve in 100 mL of water. Propose an explanation for this behavior.
10. Dimethyl sulfoxide [$(CH_3)_2SO$] is a polar liquid. Based on the information in Exercise 9, which do you think will be more soluble in it—ethanol or heptanol?

Answers

1. a homogeneous mixture
2. vinegar, dextrose IV, saline IV, coffee, tea, wine
3. A solvent is the majority component of a solution; a solute is the minority component of a solution.
4. yes. Coke or Pepsi has sugar, caffeine and carbon dioxide as solutes.
5. A solution does not have to be liquid; air is a gaseous solution, while some alloys are solid solutions (answers will vary).
6. Urine, plasma
7. a. probably soluble
   b. probably not soluble

c. probably soluble
d. probably not soluble

8.

a. probably not soluble
b. probably soluble
c. probably not soluble
d. probably soluble

9. Small alcohol molecules have strong polar intermolecular interactions, so they dissolve in water. In large alcohol molecules, the nonpolar end overwhelms the polar end, so they do not dissolve very well in water.

10. Ethanol is a smaller molecule. It will be more soluble in water than heptanol.

9.2: Concentration

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 $9.E.1$ "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 $9.E.1$ "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. 2.57×10^{-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

9.3: The Dissolution Process

Concept Review Exercise

1. Explain how the solvation process describes the dissolution of a solute in a solvent.

Answer

1. Each particle of the solute is surrounded by particles of the solvent, carrying the solute from its original phase.

Exercises

1. Describe what happens when an ionic solute like Na_2SO_4 dissolves in a polar solvent.
2. Describe what happens when a molecular solute like sucrose ($C_{12}H_{22}O_{11}$) dissolves in a polar solvent.
3. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
    a. NH_4NO_3
    b. CO_2
    c. NH_2CONH_2
    d. HCl
4. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
    a. $CH_3CH_2CH_2OH$
    b. $Ca(CH_3CO_2)_2$
    c. I_2
    d. KOH
5. Will solutions of each solute conduct electricity when dissolved?
    a. $AgNO_3$
    b. $CHCl_3$
    c. $BaCl_2$
    d. Li_2O
6. Will solutions of each solute conduct electricity when dissolved?
    a. CH_3COCH_3
    b. $N(CH_3)_3$
    c. $CH_3CO_2C_2H_5$
    d. $FeCl_2$

Answers

1. Each ion of the ionic solute is surrounded by particles of solvent, carrying the ion from its associated crystal.

2. Each sucrose molecule is surrounded by solvent molecules (attracted to each other via intermolecular forces of attraction).

3. a. electrolyte
    b. nonelectrolyte
    c. nonelectrolyte
    d. electrolyte

4. a. nonelectrolyte
    b. electrolyte
    c. nonelectrolyte
    d. electrolyte

5. a. yes
    b. no
    c. yes
    d. yes

6.

a. no
b. no
c. no
d. yes

9.4: Properties of Solutions

Concept Review Exercises

1. What are the colligative properties of solutions?
2. Explain how the following properties of solutions differ from those of the pure solvent: vapor pressure, boiling point, freezing point, and osmotic pressure.

Answers

1. Colligative properties are characteristics that a solution has that depend on the number, not the identity, of solute particles.
2. In solutions, the vapor pressure is lower, the boiling point is higher, the freezing point is lower, and the osmotic pressure is higher.

Exercises

1. In each pair of aqueous systems, which will have the lower vapor pressure?

   a. pure water or 1.0 M NaCl
   b. 1.0 M NaCl or 1.0 M $C_6H_{12}O_6$
   c. 1.0 M $CaCl_2$ or 1.0 M $(NH_4)_3PO_4$

2. In each pair of aqueous systems, which will have the lower vapor pressure?

   a. 0.50 M $Ca(NO_3)_2$ or 1.0 M KBr
   b. 1.5 M $C_{12}H_{22}O_{11}$ or 0.75 M $Ca(OH)_2$
   c. 0.10 M $Cu(NO_3)_2$ or pure water

3. In each pair of aqueous systems, which will have the higher boiling point?

   a. pure water or a 1.0 M NaCl
   b. 1.0 M NaCl or 1.0 M $C_6H_{12}O_6$
   c. 1.0 M $CaCl_2$ or 1.0 M $(NH_4)_3PO_4$

4. In each pair of aqueous systems, which will have the higher boiling point?

   a. 0.50 M $Ca(NO_3)_2$ or 1.0 M KBr
   b. 1.5 M $C_{12}H_{22}O_{11}$ or 0.75 M $Ca(OH)_2$
   c. 0.10 M $Cu(NO_3)_2$ or pure water

5. Estimate the boiling point of each aqueous solution. The boiling point of pure water is 100.0°C.

   a. 0.50 M NaCl
   b. 1.5 M Na_2SO_4
   c. 2.0 M $C_6H_{12}O_6$

6. Estimate the freezing point of each aqueous solution. The freezing point of pure water is 0.0°C.

   a. 0.50 M NaCl
   b. 1.5 M Na_2SO_4
   c. 2.0 M $C_6H_{12}O_6$

7. Explain why salt (NaCl) is spread on roads and sidewalks to inhibit ice formation in cold weather.

8. Salt (NaCl) and calcium chloride ($CaCl_2$) are used widely in some areas to minimize the formation of ice on sidewalks and roads. One of these ionic compounds is better, mole for mole, at inhibiting ice formation. Which is that likely to be? Why?

9. What is the osmolarity of each aqueous solution?

    a. 0.500 M NH_2CONH_2
    b. 0.500 M NaBr
    c. 0.500 M $Ca(NO_3)_2$

10. What is the osmolarity of each aqueous solution?

    a. 0.150 M KCl
    b. 0.450 M $(CH_3)_2CHOH$
    c. 0.500 M $Ca_3(PO_4)_2$

11. A 1.0 M solution of an unknown soluble salt has an osmolarity of 3.0 osmol. What can you conclude about the salt?

12. A 1.5 M NaCl solution and a 0.75 M $Al(NO_3)_3$ solution exist on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and the direction of solvent flow, if any, across the membrane.

Answers

1. a. 1.0 M NaCl
   b. 1.0 M NaCl
   c. 1.0 M $(NH_4)_3PO_4$

2.
    a. 1.0 M KBr
    b. 0.75 M $Ca(OH)_2$
    c. 0.10 M $Cu(NO_3)_2$

3.
    a. 1.0 M NaCl
    b. 1.0 M NaCl
    c. 1.0 M $(NH_4)_3PO_4$

4.
    a. 1.0 M KBr
    b. 0.75 M $Ca(OH)_2$
    c. 0.10 M $Cu(NO_3)_2$

5.
    a. 100.5°C
    b. 102.3°C
    c. 101°C

6.
    a. -1.9°C
    b. -8.6°C
    c. -3.8°C

7. NaCl lowers the freezing point of water, so it needs to be colder for the water to freeze.

8. $CaCl_2$ splits up into 3 ions while NaCl splits up into 2 ions only. $CaCl_2$ will be more effective.

9.
    a. 0.500 osmol
    b. 1.000 osmol
    c. 1.500 osmol

10.

a. 0.300 osmol
b. 0.450 osmol
c. 2.50 osmol

11. It must separate into three ions when it dissolves.

12. Both NaCl and $Al(NO_3)_3$ have 3.0 osmol. There will be no net difference in the solvent flow.

9.5: Chemical Equilibrium

Concept Review Exercises

1. What is chemical equilibrium?

2. What does the equilibrium constant tell us?

Answers

1. The rate of the forward reaction equals the rate of the reverse reaction.

2. The ratio of products and reactants when the system is at equilibrium.

EXERCISES

1. If the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is at equilibrium, do the concentrations of HI, H_2, and I_2 have to be equal?

2. Do the concentrations at equilibrium depend upon how the equilibrium was reached?

3. What does it mean if the K_{eq} is > 1?

4. What does it mean if the K_{eq} is < 1?

5. Does the equilibrium state depend on the starting concentrations?

6. Write an expression for the equilibrium constant K equation.

a. $PCl_5\ (g) \rightleftarrows PCl_3\ (g) + Cl_2\ (g)$

b. $2\,O_3\ (g) \rightleftharpoons 3\,O_2\ (g)$

7. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K would make this reaction most useful commercially? Explain your answer.

a. $K \approx 0.01$

b. $K \approx 1$

c. $K \approx 10.$

8. Tell whether the reactants or the products are favored at equilibrium:

a. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K = 172$

b. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K = 0.230$

c. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K = 4.6\times10^4$

d. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K = 0.050$

AnswerS

1. No, the concentrations are constant but the concentrations do not have to be equal.

2. No.

3. More products than reactants are present at equilibrium.

4. More reactants than products present at equilibrium.

5. No. The equilibrium ratio does not depend on the initial concentrations.

6.

a. $K = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

b. $K = \frac{[O_2]^3}{[O_3]^2}$

7. The answer is c. $K \approx 10$.

Since $K = \frac{[C_6H_6]^2}{[C_2H_2]^3}$ (K≈10), this means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

8.

a. products

b. reactants

c. products

d. reactants

9.6: Le Chatelier's Principle

Concept Review Exercises

1. Define Le Chatelier’s principle.

2. List the three factors types of changes that can disturb the equilibrium of a system.

Answers

1. Le Chatelier’s principle states that a system at equilibrium is disturbed, it will respond in a way to minimize the disturbance.

2. temperature, change in amount of substance, change in pressure through change in volume

EXERCISES

1. How will each change affect the reaction?

$PCl_5(g)$ + heat ⇌$PCl_3(g)$ + $Cl_2(g)$

a. Addition of PCl_5
b. Addition of Cl_2
c. Removal of PCl_3
d. Increasing temperature
e. Decreasing temperature
f. Decreasing volume

2. How will each change affect the reaction?

$HNO_2(aq)$ ⇌$H^+(aq)$ + $NO_2^-(aq)$

a. Removal of HNO_2
b. Addition of HCl (i.e. adding more H^+)
c. Increasing volume
d. Decreasing volume

e. Removal of NO_2^-
f. Addition of OH^- (which will react with and remove H^+)

3. How will each change affect the reaction?

$CO_2(g) + C(s) \rightleftharpoons 2CO(g)\ \Delta H=172.5kJ$

a. Addition of CO_2
b. Removal of CO_2
c. Increasing temperature
d. Decreasing temperature
e. Increasing volume
f. Addition of CO

4. How will each change affect the reaction?

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)\ \Delta H=-9.48kJ$

a. Addition of H_2
b. Removal of H_2
c. Increasing temperature
d. Decreasing temperature
e. Increasing volume
f. Decreasing volume

AnswerS

1.

a. shift right
b. shift left
c. shift right
d. shift right
e. shift left
f. shift left

2.

a. shift left
b. shift left
c. no effect
d. no effect
e. shift right
f. shift right

3.

a. shift right
b. shift left
c. shift right
d. shift left
e. shift right
f. shift left

4.

a. shift right
b. shift left
c. shift left

d. shift right
e. no effect
f. no effect

9.7: Osmosis and Diffusion

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

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?

2. Two solutions with different concentrations and compositions are separated by a semipermeable membrane. The left-hand solution is a .50 M solution of $MgSO_4$, while the right-hand solution contains $CaCl_2$ at a concentration of .40 M. Determine the direction of the flow of solvent, left or right.

3. Given the following situations, wherein two tanks of different solutions are separated by a semipermeable membrane, determine the direction of the flow of solvent (water).

a. Solution A contains a 0.40 M concentration of $CaCl_2$, while Solution B contains a 0.45 M concentration of KI

b. Solution A contains a 1.00 M concentration of NH_4Cl, while Solution B contains a 1.00 M concentration of CH_2O

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.

7. What makes up the "head" region of a phospholipid? Is it hydrophobic or hydrophilic?

8. What makes up the "tail" region of a phospholipid? Is it hydrophobic or hydrophilic?

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

2. Water (solvent) flows from left to right.

3.

a. Water flows from Solution B to Solution A.

b. Water flows from Solution B to Solution A.

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.

7. The "head" region is a phosphate group and it is hydrophilic.

8. The "tail" is a hydrocarbon tail and it is hydrophobic.

Contributors

-
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Additional Exercises

1. Calcium nitrate reacts with sodium carbonate to precipitate solid calcium carbonate:

$$Ca(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + NaNO_{3(aq)} \tag{9.E.1}$$

   a. Balance the chemical equation.
   b. How many grams of Na_2CO_3 are needed to react with 50.0 mL of 0.450 M $Ca(NO_3)_2$?
   c. Assuming that the Na_2CO_3 has a negligible effect on the volume of the solution, find the osmolarity of the $NaNO_3$ solution remaining after the $CaCO_3$ precipitates from solution.

2. The compound HCl reacts with sodium carbonate to generate carbon dioxide gas:

$$HCl_{(aq)} + Na_2CO_{3(aq)} \rightarrow H_2O_{(\ell)} + CO_{2(g)} + NaCl_{(aq)} \tag{9.E.2}$$

   a. Balance the chemical equation.
   b. How many grams of Na_2CO_3 are needed to react with 250.0 mL of 0.755 M HCl?
   c. Assuming that the Na_2CO_3 has a negligible effect on the volume of the solution, find the osmolarity of the NaCl solution remaining after the reaction is complete.

3. Estimate the freezing point of concentrated aqueous HCl, which is usually sold as a 12 M solution. Assume complete ionization into H^+ and Cl^- ions.

4. Estimate the boiling point of concentrated aqueous H_2SO_4, which is usually sold as an 18 M solution. Assume complete ionization into H^+ and HSO_4^- ions.

5. Seawater can be approximated by a 3.0% m/m solution of NaCl in water. Determine the molarity and osmolarity of seawater. Assume a density of 1.0 g/mL.

6. Human blood can be approximated by a 0.90% m/m solution of NaCl in water. Determine the molarity and osmolarity of blood. Assume a density of 1.0 g/mL.

7. How much water must be added to 25.0 mL of a 1.00 M NaCl solution to make a resulting solution that has a concentration of 0.250 M?

8. Sports drinks like Gatorade are advertised as capable of resupplying the body with electrolytes lost by vigorous exercise. Find a label from a sports drink container and identify the electrolytes it contains. You should be able to identify several simple ionic compounds in the ingredients list.
9. Occasionally we hear a sensational news story about people stranded in a lifeboat on the ocean who had to drink their own urine to survive. While distasteful, this act was probably necessary for survival. Why not simply drink the ocean water? (Hint: See Exercise 5 and Exercise 6 above. What would happen if the two solutions in these exercises were on opposite sides of a semipermeable membrane, as we would find in our cell walls?)

Answers

1.
   a. $Ca(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaNO_3(aq)$
   b. 2.39 g
   c. 1.80 osmol
2.
   a. $2HCl\ (aq) + Na_2CO_3(aq) \rightarrow H_2O(\ell) + CO_2(g) + 2NaCl\ (aq)$
   b. 10.0 g
   c. 1.51 M
3. −45.6°C
4. 118°C
5. 0.513 M; 1.026 osmol
6. molarity = 0.15 M; osmolarity = 0.31 M
7. 75.0 mL
8. magnesium chloride, calcium chloride (answers may vary)
9. The osmotic pressure of seawater is too high. Drinking seawater would cause water to go from inside our cells into the more concentrated seawater, ultimately killing the cells.

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9.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

10: Acids and Bases

10.0: Prelude to Acids and Bases
10.1: Acids and Bases Definitions
10.2: Acid and Base Strength
10.3: Water as Both an Acid and a Base
10.4: Measuring Acidity in Aqueous Solutions- The pH Scale
10.5: Working with pH
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10.7: Titration

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10.0: Prelude to Acids and Bases

One of the most concentrated acids in the body is stomach acid, which can be approximated as a 0.05 M hydrochloric acid solution. Special cells in the stomach wall secrete this acid, along with special enzymes, as part of the digestion process. In a laboratory, a 0.05 M solution of hydrochloric acid would dissolve some metals. How does the stomach survive the presence of such a reactive acid?

Actually, the stomach has several mechanisms for withstanding this chemical onslaught. First, the lining of the stomach is coated with a thin layer of mucus that contains some bicarbonate ions (HCO_3^-). These react with the hydrochloric acid to produce water, carbon dioxide, and harmless chloride ions. If any acid penetrates through the mucus, it can attack the surface layer of stomach cells, called the *gastric epithelium*. Cells in the gastric epithelium are being constantly shed, so damaged cells are quickly removed and replaced with healthy cells.



Figure 10.0.1: Stomach with acidic digestive juices. (CC BY-SA 4.0; BruceBlaus).

However, if the gastric epithelium is destroyed faster than it can be replaced, the acid may reach the wall of the stomach, resulting in ulcers. If an ulcer grows large enough, it can expose blood vessels in the stomach wall, causing bleeding. In extreme situations, the loss of blood through a severe ulcer can threaten a person's health.

Ulcers can also result from the presence of a certain bacterium—*Helicobacter pylori*—in the stomach. The mechanism for this ulcer formation is not the same as that for ulcers caused by stomach acid and is not completely understood. However, there are two main treatments for ulcers: (1) *antacids* to react chemically with excess hydrochloric acid in the stomach and (2) *antibiotics* to destroy the *H. pylori* bacteria in the stomach.

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10.1: Acids and Bases Definitions

Learning Objectives

- Identify an Arrhenius acid and an Arrhenius base.
- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

There are three major classifications of substances known as acids or bases. The theory developed by Svante Arrhenius in 1883, the Arrhenius definition, states that an acid produces hydrogen ions, H^+, in solution and a base produces hydroxide ions, OH^-. Later, two more sophisticated and general theories were proposed. These theories are the Brønsted-Lowry and Lewis definitions of acids and bases. This section will cover the Arrhenius and Brønsted-Lowry theories; Lewis theory is discussed elsewhere.

The Arrhenius Theory of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. An **Arrhenius acid** is a compound that *increases the concentration* of H^+ ions that are present when added to water. These H^+ ions form the **hydronium ion** (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$\mathrm{HCl\,(aq)} \rightarrow \mathrm{H^+\,(aq) + Cl^-\,(aq)} \tag{10.1.1}$$

In this reaction, hydrochloric acid (HCl) dissociates completely into hydrogen (H^+) and chloride (\Cl^{-}\)) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$\mathrm{HCl\,(aq) + H_2O(\ell)} \rightarrow \mathrm{H_3O^+\,(aq) + Cl^-\,(aq)} \tag{10.1.2}$$

An **Arrhenius base** is a compound that *increases the concentration* of OH^- ions that are present when added to water. The dissociation is represented by the following equation:

$$\mathrm{NaOH\,(aq)} \rightarrow \mathrm{Na^+\,(aq) + OH^-\,(aq)} \tag{10.1.3}$$

In this reaction, sodium hydroxide (NaOH) disassociates into sodium (Na^+) and hydroxide (OH^-) ions when dissolved in water, thereby releasing OH^- ions into solution.

> *Arrhenius acids are substances which produce hydrogen ions in solution and Arrhenius bases are substances which produce hydroxide ions in solution.*

Limitations to the Arrhenius Theory

The Arrhenius theory has many more limitations than the other two theories. The theory does not explain the weak base ammonia (NH_3), which in the presence of water, releases hydroxide ions into solution, but does not contain OH^- itself. The Arrhenius definition of acid and base is also limited to aqueous (i.e., water) solutions.

The Brønsted-Lowry Theory of Acids and Bases

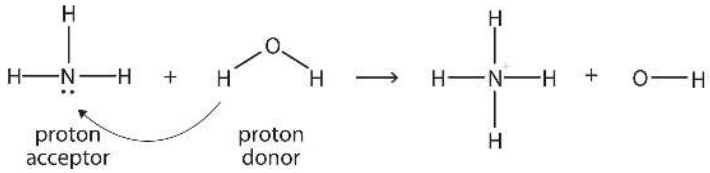
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

> *A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.*

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_3\,(aq) + H_2O(\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \tag{10.1.4}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



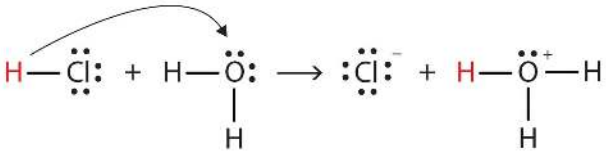
Because the water molecule *donates* a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which *accepts* the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen ion, we remove the electron, leaving a bare proton. Do we really have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl\,(g) + H_2O(\ell)\ \rightarrow H_3O^+\,(aq)\ Cl^-\,(aq) + H_3O^+\,(aq) \tag{10.1.5}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; the hydrogen ion acceptor, H_2O is a Brønsted-Lowry base. So HCl is an acid not just in the Arrhenius sense, but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

Note: Acid and Base Definitions

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.
- **All** Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

Example 10.1.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2\,(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3{}^+\,(aq) + OH^-\,(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

? Exercise 10.1.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$H_2PO_4{}^- + H_2O \rightleftharpoons HPO_4{}^{2-} + H_3O^+ \tag{10.1.6}$$

Answer

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H_2O

? Exercise 10.1.2

Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. HPO_4^{2-}
c. H_3PO_4
d. NH_4^+
e. $CH_3NH_3^+$

Answer

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an H^+. This eliminates HCl, H_3PO_4, $NH_4{}^+$ and $CH_3NH_3{}^+$ because they are Bronsted-Lowry acids. They all give away protons. In the case of $HPO_4{}^{2-}$, consider the following equation:

$$HPO_4{}^{2-}\,(aq) + H_2O\,(l) \rightarrow PO_4{}^{3-}\,(aq) + H_3O^+\,(aq)$$

Here, it is clear that HPO_4^{2-} is the acid since it donates a proton to water to make H_3O^+ and PO_4^{3-}. Now consider the following equation:

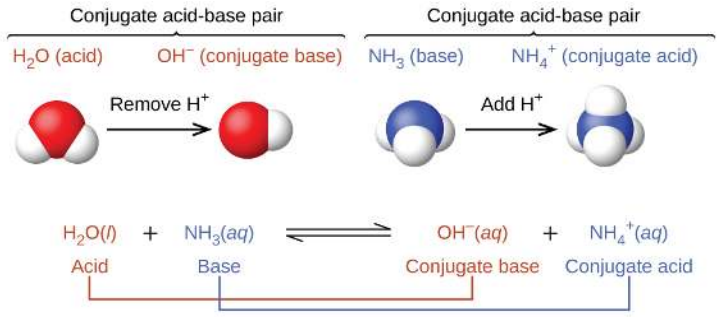
$$HPO_4{}^{2-}\,(aq) + H_2O\,(l) \rightarrow H_2PO_4{}^- + OH^-\,(aq)$$

In this case, HPO_4^{2-} is the base since it accepts a proton from water to form $H_2PO_4^-$ and OH^-. Thus, HPO_4^{2-} is an acid and base together, making it amphoteric.

Since HPO_4^{2-} is the only compound from the options that can act as a base, the answer is **(b) HPO_4^{2-}.**

Conjugate Acid-Base Pair

In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, $NH_4{}^+$:



In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.

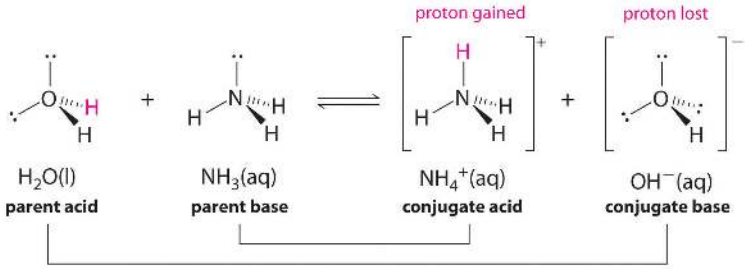


Figure 10.1.1. The pairing of parent acids and bases with conjugate acids and bases.

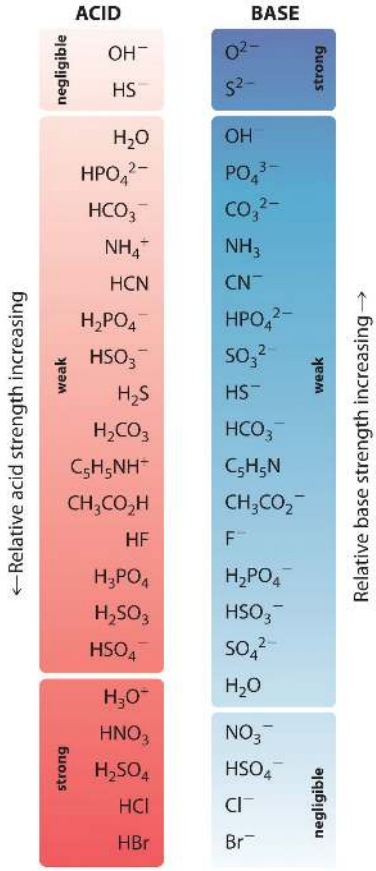


Figure 10.1.2: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Example 10.1.2

Identify the conjugate acid-base pairs in this equilibrium.

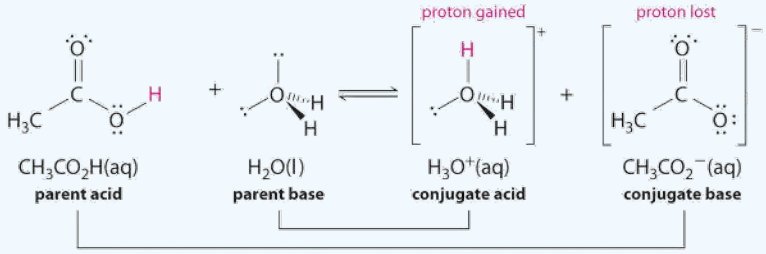
$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 10.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 10.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

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10.2: Acid and Base Strength

Learning Objectives

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.

Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider $\mathrm{HCl(aq)}$. When HCl is dissolved in $\mathrm{H_2O}$, it completely **dissociates** (separates) into $\mathrm{H^+(aq)}$ and $\mathrm{Cl^-(aq)}$ ions; all the HCl molecules become ions:

$$\mathrm{HCl} \xrightarrow{100\,\%} \mathrm{H^+(aq) + Cl^-(aq)} \tag{10.2.1}$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $\mathrm{HC_2H_3O_2}$ is an example of a weak acid:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq) \tag{10.2.2}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq) \tag{10.2.3}$$

As it turns out, there are very few strong acids, which are given in Table 10.2.1. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

> *Any acid that dissociates 100% into ions is called a strong acid. If it does not dissociate 100%, it is a weak acid.*

Figure 10.2.1: Some of the common strong acids and bases are listed here.

Strong Acids		Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

Strong and Weak Bases

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (Table 10.2.1); any base not listed is a weak base. All strong bases are $\mathrm{OH^-}$ compounds. So a base based on some other mechanism, such as $\mathrm{NH_3}$ (which does not contain $\mathrm{OH^-}$ ions as part of its formula), will be a weak base.

Example 10.2.1: Identifying Strong and Weak Acids and Bases

Identify each acid or base as strong or weak.

a. HCl
b. $\mathrm{Mg(OH)_2}$

c. C_5H_5N

Solution

a. Because HCl is listed in Table 10.2.1, it is a strong acid.

b. Because $Mg(OH)_2$ is listed in Table 10.2.1, it is a strong base.

c. The nitrogen in C_5H_5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Exercise 10.2.1

Identify each acid or base as strong or weak.

a. $RbOH$

b. HNO_2

Answer

a. strong base

b. weak acid

Example 10.2.2: Characterizing Base Ionization

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

Solution

This is an ionic compound of Ca^{2+} ions and OH^- ions. When an ionic compound dissolves, it separates into its constituent ions:

$$Ca(OH)_2 \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$$

Because $Ca(OH)_2$ is listed in Table 10.2.1, this reaction proceeds 100% to products.

Exercise 10.2.2

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer a

The reaction is as follows:

$$HN_3 \longrightarrow H^+(aq) + {N_3}^-(aq)$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Looking Closer: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for hydrochloric acid [$HCl(aq)$]. Vinegar has already been mentioned as a dilute solution of acetic acid [$HC_2H_3O_2(aq)$]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is ammonia (NH_3), which is found in numerous cleaning products. As we mentioned previously, ammonia is a base because it increases the hydroxide ion concentration by reacting with water:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq) \tag{10.2.4}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.



Figure 10.2.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for sodium hydroxide, although it is also used as a synonym for potassium hydroxide. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and form a clog in a pipe. Unfortunately, lye can also attack tissues and other substances in our bodies. Thus, when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners use peroxide compounds to react on the materials in the clog and clear the drain.

Chemical Equilibrium in Weak Acids and Bases

Ionization of weak acids or bases are reversible reactions, which means the forward and reverse reactions occur and eventually reach equilbrium. For example, the ionization of the weak acid $HC_2H_3O_2\,(aq)$ is as follows:

$$HC_2H_3O_2\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \tag{10.2.5}$$

The reverse process also begins to occur:

$$H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) + H_2O(\ell) \tag{10.2.6}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$HC_2H_3O_2\,(aq) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \tag{10.2.7}$$

The $\rightleftharpoons$ implies that both the forward and reverse reactions are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

Example 10.2.3: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. HNO_2(aq)
b. C_5H_5N(aq)

Solution

a. $HNO_2(aq) + H_2O(\ell) \leftrightarrows NO_2^-(aq) + H_3O^+(aq)$
b. $C_5H_5N(aq) + H_2O(\ell) \leftrightarrows C_5H_5NH^+(aq) + OH^-(aq)$

Exercise 10.2.3

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HF_{(aq)}$
b. $AgOH_{(aq)}$
c. $CH_3NH_2(aq)$

Answer

a. $HF(aq) + H_2O(\ell) \leftrightarrows F^-(aq) + H_3O^+(aq)$

b. $AgOH(aq) \leftrightarrows Ag^+(aq) + OH^-(aq)$

c. $CH_3NH_2(aq) + H_2O(\ell) \leftrightarrows CH_3NH_3^+(aq) + OH^-(aq)$

Strengths of Conjugate Acid and Base Pairs

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 10.2.2).

The first six acids in Figure 10.2.2 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 10.2.2 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and non-ionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 10.2.2 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

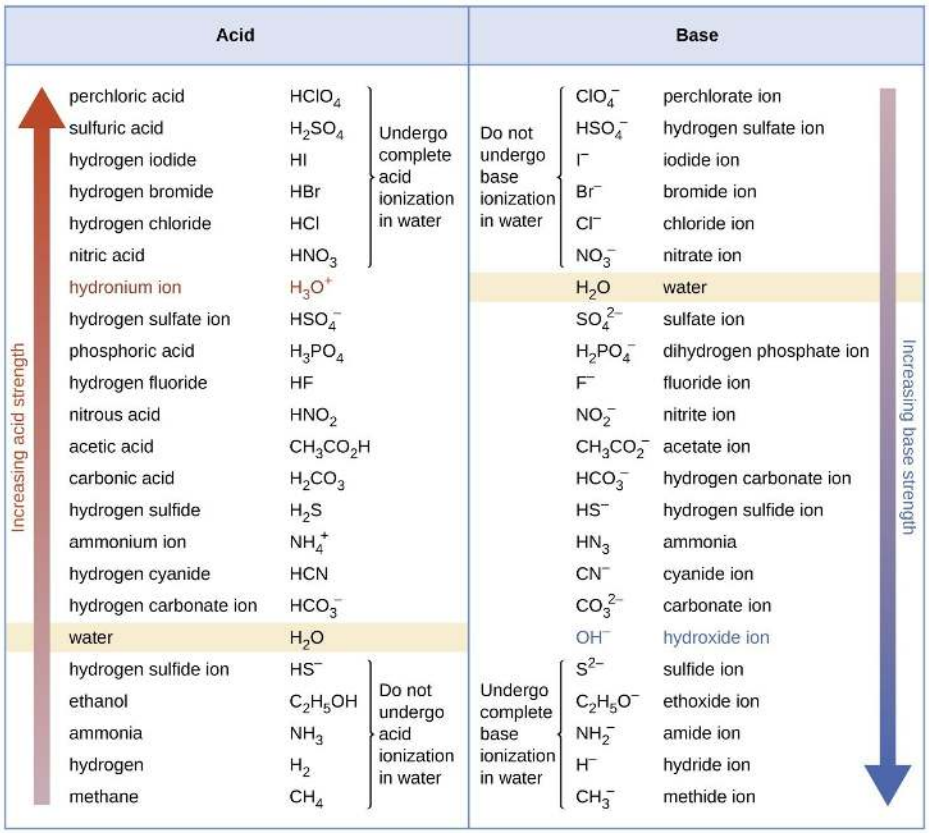


Figure 10.2.2: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 10.2.2. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Key Takeaways

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.

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10.3: Water as Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.
- Define and use the ion product constant for water, K_w, to calculate concentrations of H_3O^+ and OH^- in aqueous solutions.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$HCl + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{10.3.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion, a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{10.3.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{10.3.3}$$

This process is called the **autoionization of water** (Figure 10.3.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

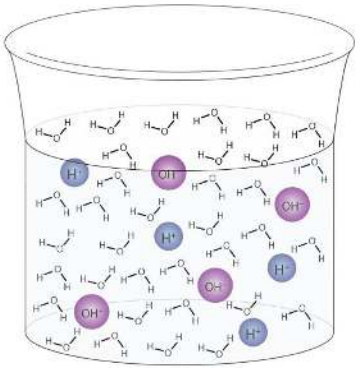


Figure 10.3.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

Example 10.3.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $OH^-(aq)$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

? Exercise 10.3.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Dissociation of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{10.3.4}$$

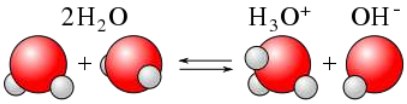


Figure 10.3.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{10.3.5}$$

We often use the simplified form of the reaction:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_w = [H^+][OH^-]$$

The **ion-product constant for water (K_w)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be *neutral*. To find the molarity of each ion, the square root of K_w is taken.

$$[H^+] = [OH^-] = 1.0\times10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[H^+]\times[OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of H^+ or $[H^+]$ is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- or $[OH^-]$ is greater than 1.0×10^{-7} M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This increases the concentration of H^+ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

$$HCl\,(g) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$$

is forced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$

The increase in concentration of the OH^- ions will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, $[H^+]$ is greater than $[OH^-]$.
- For basic solutions, [OH−] is greater than $[H^+]$.
- For neutral solutions, $[H_3O^+]$ = [OH−] = 1.0×10^{-7}M

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$), you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{10.3.6}$$

Example 10.3.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^{-3} M HCl?

Solution

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

Known

- [HCl] = 2.0×10^{-3} M
- Kw = 1.0×10^{-14}

Unknown

- $[H^+]$=?M
- $[OH^-]$=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl− ion. The concentration of OH− can then be determined from the [H+] and Kw.

Step 2: Solve.

$$[H^+]=2.0\times10^{-3}\,M$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\,M$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

? Exercise 10.3.2

Sodium hydroxide (NaOH) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer

$[OH^-] = 0.001M$ or $1 \times 10^{-3}M$; $[H^+]=1\times10^{-11}M$.

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is H_2O acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some NH_4^+ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is H_2O acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

Answers

1. base
2. acid
3. acid
4. base

5. When water ionizes, equal amounts of H^+ (acid) and OH^- (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

[SIDE NOTE: It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.]

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10.4: Measuring Acidity in Aqueous Solutions- The pH Scale

Learning Objectives

- Define the pH scale and use it to describe acids and bases.
- Calculate the pH of a solution from $[H_3O^+]$ and $[OH^-]$.

Knowing the amount of acid and base in solutions is extremely important for a wide variety of applications ranging from brewing beer or wine to studying the effects of ocean acidification to health and medicine. Scientists are good at calculating and measuring the concentration of hydronium in a solution, however, there is a more convenient way to make comparisons between solutions – *the pH scale*.

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure 10.4.1 illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the *negative* log of $[H_3O^+]$, which will give a positive value for pH.

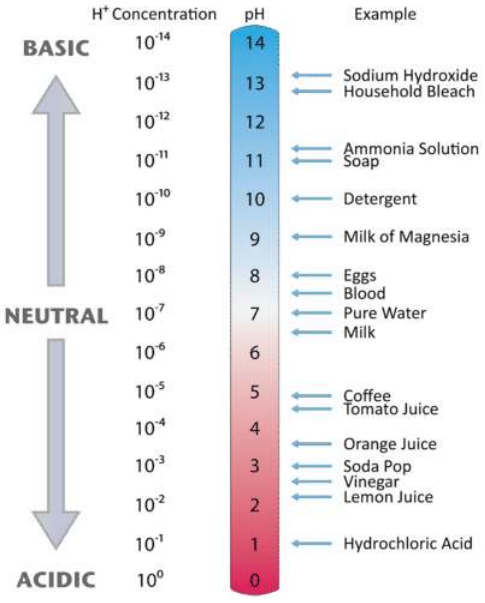


Figure 10.4.1: The relationaship between [H+] and pH *values for several common materials.*

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in Table \(\PageIndex{1}.

Table 10.4.1: Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	pH < 7
neutral	$[H^+] = [OH^-]$	pH = 7
basic	$[H^+] < [OH^-]$	pH > 7

Example 10.4.1

Find the pH, given the $[H^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

pH = - log $[H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. pH = - log $[1 \times 10^{-3}]$ = 3.0 (1 decimal place since 1 has 1 significant figure)
b. pH = - log $[2.5 \times 10^{-11}]$ = 10.60 (2 decimal places since 2.5 has 2 significant figures)
c. pH = - log $[4.7 \times 10^{-9}]$ = 8.33 (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

Exercise 10.4.1

Find the pH, given $[H^+]$ of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7} M

Answer

a. 3.24

b. 7.00

Figure 10.4.2 lists the pH of several common solutions. The most *aci*dic among the listed solutions is 1 M HCl with the lowest pH value (0.0): battery acid is the next most acidic solution with a pH value of 0.3. The most *basic* is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

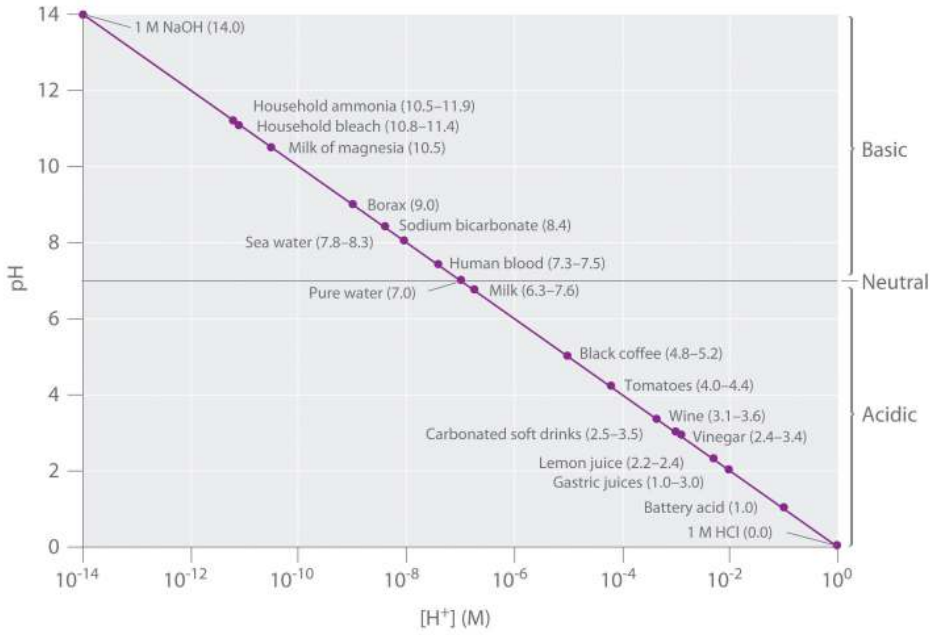


Figure 10.4.2: A Plot of pH versus $[H^+]$ for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

Example 10.4.2

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Solution

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

Exercise 10.4.2

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with pH = 7.4
b. household ammonia with pH = 11.0
c. cherries with pH = 3.6

Answer

a. slightly basic

b. basic

c. acidic

Measuring pH

Tools have been developed that make the measurement of pH simple and convenient. For example, pH paper (Figure 10.4.3)consists of strips of paper impregnated with one or more **acid-base indicators**, which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH

paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the H^+ ion concentration (Figure 10.4.3).



Figure 10.4.3: Ways to measure pH. (left) These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center strip is pH range 5-10 and shows results of a 6.97 buffer solution sample; the strip on the right measures a broad range (pH 1-14) and shows results of a 10% bleach water solution sample. This image can be enlarged by clicking on it. (right) These three meters and probes can measure pH (left) and electrical conductivity (center and right). Photos by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).

Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq) \tag{10.4.1}$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3{}^-\,(aq) \tag{10.4.2}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq) \tag{10.4.3}$$

$$H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4{}^-\,(aq) \tag{10.4.4}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the

destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 10.4.4). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

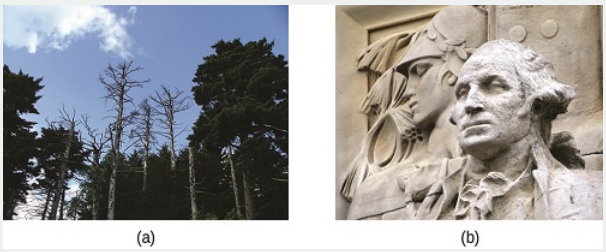


Figure 10.4.4: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

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10.5: Working with pH

Learning Objectives

- Calculate pH from $[H_3O^+]$ and $[H_3O^+]$ from pH.

Calculating pH from Hydronium Concentration

The pH of solutions can be determined by using logarithms as illustrated in the next example for stomach acid. Stomach acid is a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$, what is the pH of the solution?

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

Logarithms

To get the **log value** on your calculator, enter the number (in this case, the hydronium ion concentration) first, then press the LOG key.

If the number is 1.0 x 10^{-5} (for $[H_3O^+]$ = 1.0 x 10^{-5} M) you should get an answer of "-5".

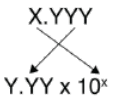
If you get a different answer, or an error, try pressing the LOG key before you enter the number.

Example 10.5.2: Converting Ph to Hydronium Concentration

Find the pH, given the $[H_3O^+]$ of the following:

a. 1 ×10^{-3} M
b. 2.5 ×10^{-11} M
c. 4.7 ×10^{-9} M

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: a. $[H_3O^+]$ =1 × 10^{-3} M b. $[H_3O^+]$ =2.5 ×10^{-11} M c. $[H_3O^+]$ = 4.7 ×10^{-9} M Find: ? pH
Plan the problem.	Need to use the expression for pH (Equation ???). pH = - log $[H_3O^+]$
Calculate.	Now substitute the known quantity into the equation and solve. a. pH = - log [1 × 10^{-3}] = 3.0 (1 decimal places since 1 has 1 significant figure) b. pH = - log [2.5 ×10^{-11}] = 10.60 (2 decimal places since 2.5 has 2 significant figures) c. pH = - log [4.7 ×10^{-9}] = 8.30 (2 decimal places since 4.7 has 2 significant figures) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

Exercise 10.5.2

Find the pH, given $[H_3O^+]$ of the following:

a. 5.8 ×10^{-4} M
b. 1.0×10^{-7}

Answer a

3.22

Answer b

7.00

Calculating Hydronium Concentration from pH

Sometimes you need to work "backwards"—you know the pH of a solution and need to find $[H_3O^+]$, or even the concentration of the acid solution. How do you do that? To convert pH into $[H_3O^+]$ we solve Equation ??? for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[H_3O^+] = \text{antilog}(-pH) \tag{10.5.1}$$

or

$$[H_3O^+] = 10^{-pH} \tag{10.5.2}$$

As mentioned above, different calculators work slightly differently—make sure you can do the following calculations using ***your*** calculator.

Calculator Skills

We have a solution with a pH = 8.3. What is $[H_3O^+]$?

With some calculators you will do things in the following order:

1. Enter 8.3 as a negative number (use the key with both the +/- signs, not the subtraction key).
2. Use your calculator's 2nd or Shift or INV (inverse) key to type in the symbol found above the LOG key. The shifted function should be 10^x.
3. You should get the answer **5.0×10^{-9}**.

Other calculators require you to enter keys in the order they appear in the equation.

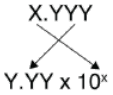
1. Use the Shift or second function to key in the 10^x function.
2. Use the +/- key to type in a negative number, then type in 8.3.
3. You should get the answer **5.0×10^{-9}**.

If neither of these methods work, try rearranging the order in which you type in the keys. Don't give up—you must master your calculator!

Example 10.5.3: Calculating Hydronium Concentration from pH

Find the hydronium ion concentration in a solution with a pH of 12.6. Is this solution an acid or a base? How do you know?

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH = 12.6 Find: $[H_3O^+]$ = ? M
Plan the problem.	Need to use the expression for $[H_3O^+]$ (Equation 10.5.2). $[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$
Calculate.	Now substitute the known quantity into the equation and solve. $[H_3O^+]$ = antilog (12.60) = 2.5 x 10^{-13} M (2 significant figures since 4.7 has 12.60 2 decimal places) or $[H_3O^+] = 10^{-12.60} = 2.5 \times 10^{-13}$ M (2 significant figures since 4.7 has 12.60 2 decimal places) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

Exercise 10.5.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

Answer

1.5×10^{-8} M

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10.6: Buffers

Learning Objectives

- To define *buffer* and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have a marked chemical activity. 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 [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. A *buffer* (or *buffered*) solution is one that resists a change in its pH when H^+ or OH^- ions are added or removed owing to some other reaction taking place in the same solution. Buffers do so by being composed of certain pairs of solutes: either a **weak acid plus its conjugate base** or a **weak base plus its conjugate acid**.

For example, a buffer can be composed of dissolved **acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate** ($NaC_2H_3O_2$). Sodium acetate is a salt that dissociates into sodium ions and acetate ions in solution. For as long as acetic acid and acetate ions are present in significant amounts a solution, this can resist dramatic pH changes. Another example of a buffer is a solution containing **ammonia (NH_3, a weak base) and ammonium chloride** (NH_4Cl). Ammonium acetate is also a salt that dissociates into ammonium ions and chloride ions in solution. The presence of ammonium ions with ammonia molecules satisfies the requisite condition for a buffer solution.

How Buffers Work

The essential component of a buffer system is a **conjugate acid-base pair** whose concentration is fairly high in relation to the concentrations of added H^+ or OH^- it is expected to buffer against. Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of OH^-(aq) ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_2\,(aq) + OH^-\,(aq) \longrightarrow H_2O(\ell) + C_2H_3O_2^-\,(aq) \tag{10.6.1}$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

> Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

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 hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+\,(aq) + C_2H_3O_2^-\,(aq) \longrightarrow HC_2H_3O_2\,(aq) \tag{10.6.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 10.6.1 illustrates both actions of a buffer.

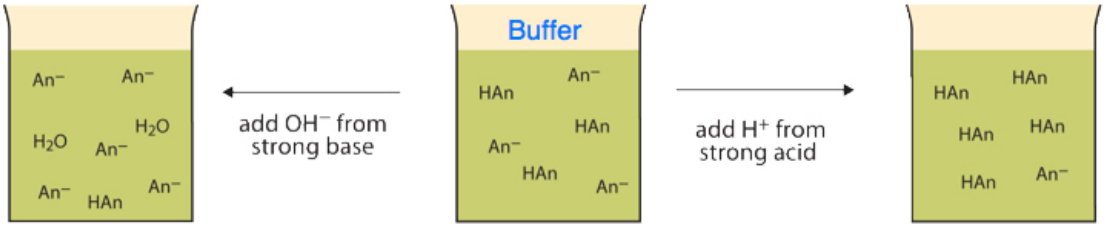


Figure 10.6.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

A simple buffer system might be a 0.2 *M* solution of sodium acetate; the conjugate pair here is acetic acid HAc and its conjugate base, the acetate ion Ac^-. The idea is that this conjugate pair "pool" will be available to gobble up any small ($\leq 10^{-3}$ *M*) addition of H+ or OH^- that may result from other processes going on in the solution.

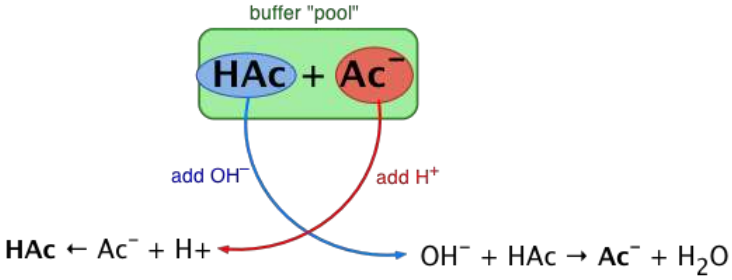


Figure 10.6.2: How HAc/Ac buffer works

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all 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 solute dissolved in them to start with have larger capacities, as might be expected.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_{3(aq)} + H^+_{(aq)} \rightarrow NH^+_{4(aq)} \tag{10.6.3}$$

while the ammonium ion [NH_4^+(aq)] can react with any hydroxide ions introduced by strong bases:

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightarrow NH_{3(aq)} + H_2O_{(\ell)} \tag{10.6.4}$$

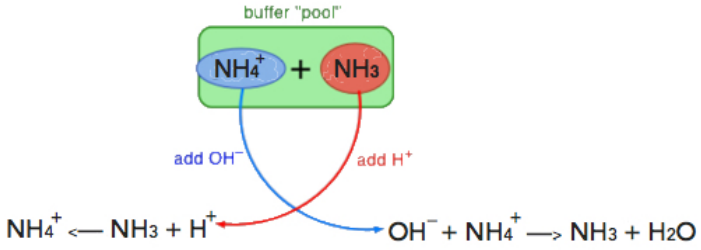


Figure 10.6.3: How NH_4^+/NH_3 buffer works

Example 10.6.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $HCHO_2$ and $NaCHO_2$
b. HCl and NaCl
c. CH_3NH_2 and CH_3NH_3Cl

d. NH_3 and NaOH

Solution

a. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is a salt supplying —formate ion (CHO_2^-), the conjugate base of $HCHO_2$. The combination of these two solutes would make a buffer solution.
b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
c. Methylamine (CH_3NH_2) is like ammonia, a weak base. The compound CH_3NH_3Cl is a salt supplying $CH_3NH_3^+$, the conjugate acid of CH_3NH_2. The combination of these two solutes would make a buffer solution.
d. Ammonia (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 10.6.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $NaHCO_3$ and NaCl
b. H_3PO_4 and NaH_2PO_4
c. NH_3 and $(NH_4)_3PO_4$
d. NaOH and NaCl

Answer

b. H_3PO_4 (weak acid) and $H_2PO_4^-$ (conjugate base of H_3PO_4) make a buffer.

c. NH_3 (weak base) and NH_4^+ (conjugate acid of NH_3) make a buffer

Food and Drink App: 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 10.5.1, 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.

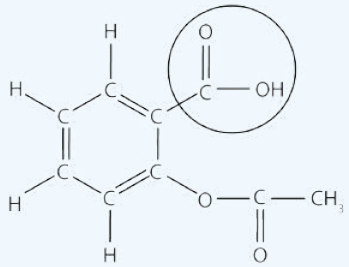


Figure 10.6.4 The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

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 is here to stay.

Buffer solutions are essential components of all living organisms.

- Our blood is buffered to maintain a pH of 7.4 that must remain unchanged as metabolically-generated CO_2 (carbonic acid) is added and then removed by our lungs.
- Buffers in the oceans, in natural waters such as lakes and streams, and within soils help maintain their environmental stability against acid rain and increases in atmospheric CO_2.
- Many industrial processes, such as brewing, require buffer control, as do research studies in biochemistry and physiology that involve enzymes, are active only within certain pH ranges.

The pH in living systems (Figure \(\PageIndex{1}\)) is maintained by buffer systems.

Table 7.3.2: pH in Living Systems

Compartment	pH
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

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 [H_2CO_3 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.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq) + \mathrm{H_3O}^+(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, HCO_3^-, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. HCl and NaCl
    2. HNO_2 and $NaNO_2$
    3. NH_4NO_3 and HNO_3
    4. NH_4NO_3 and NH_3
4. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. H_3PO_4 and Na_3PO_4
    2. $NaHCO_3$ and Na_2CO_3
    3. $NaNO_3$ and $Ca(NO_3)_2$
    4. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?

8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.
3. 1. not a buffer
   2. buffer
   3. not a buffer
   4. buffer

4. 1. not a buffer

2. buffer

3. not a buffer

4. not buffer

5. 3b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; 3d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$
6. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow HCO3^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$;
7. Buffers can be made by combining H_3PO_4 and $H_2PO_4^-$, $H_2PO_4^-$ and HPO_4^{2-}, and HPO_4^{2-} and PO_4^{3-}.
8. NaBr splits up into two ions in solution, Na^+ and Br^-. Na^+ will not react with any added base knowing that NaOH is a strong base. Br- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.
9. $Mg(NO_3)_2$ includes two types of ions, Mg^{2+} and NO_3^-. $Mg(OH)_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). HNO_3 is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $Mg(NO_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

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10.7: Titration

Learning Objectives

- Describe a titration experiment.
- Explain what an indicator does.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

In a titration, one reagent has a known concentration or amount, while the other reagent has an unknown concentration or amount. Typically, the known reagent (the **titrant**) is added to the unknown quantity and is dissolved in solution. The unknown amount of substance (the **analyte**) may or may not be dissolved in solution (but usually is). The titrant is added to the analyte using a precisely calibrated volumetric delivery tube called a burette (also spelled buret; see Figure 10.7.1). 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 10.7.1 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 10.7.1

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:

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

$$\text{\# moles } HNO_3 = (0.04402\text{ L})(0.0885\text{ M}) = 0.00390\text{ mol } HNO_3$$

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390\ \cancel{mol\ HNO_3} \times \frac{1\ mol\ Ca(OH)_2}{2\ \cancel{mol\ HNO_3}} = 0.00195\ mol\ Ca(OH)_2$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195\ \cancel{mol\ Ca(OH)_2} \times \frac{74.1\ g\ Ca(OH)_2}{\cancel{mol\ Ca(OH)_2}} = 0.144\ g\ Ca(OH)_2$$

? Exercise 10.7.1

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.

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CHAPTER OVERVIEW

11: Organic Chemistry

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.

- 11.0: Prelude to Organic Chemistry
- 11.1: Hydrocarbons
- 11.2: Branched Hydrocarbons
- 11.3: Alkyl Halides and Alcohols
- 11.4: Other Oxygen-Containing Functional Groups
- 11.5: Other Nitrogen and Sulfur-Containing Functional Groups
- 11.6: Polymers
- 11.E: Organic Chemistry (Exercises)

Template:HideTOC

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11.0: Prelude to Organic Chemistry

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 11.0.1: 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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11.1: Hydrocarbons

Learning Objectives

- Identify alkanes, alkenes, alkynes, and aromatic compounds.
- List some properties of hydrocarbons.

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called **hydrocarbons**. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons.

Aliphatic hydrocarbons are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are hydrocarbons that contain at least one C–C double bond, and **Alkynes** are hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called *cycloalkanes* (or *cycloalkenes* or *cycloalkynes*).

Aromatic hydrocarbons have a special six-carbon ring called a *benzene* ring. Electrons in the benzene ring have special energetic properties that give benzene physical and chemical properties that are markedly different from alkanes. Originally, the term *aromatic* was used to describe this class of compounds because they were particularly fragrant. However, in modern chemistry the term *aromatic* denotes the presence of a six-membered ring that imparts different and unique properties to a molecule.

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:

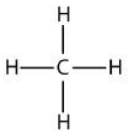


Figure 11.1.1 - Three-Dimensional Representation of Methane.

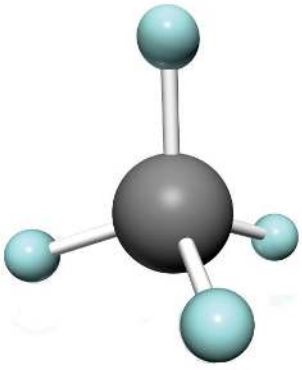
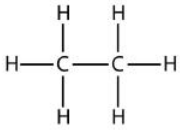
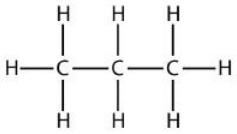


Figure 11.1.1 Three-Dimensional Representation of Methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron.

The next-largest alkane has two C atoms that are covalently bonded to each other. For each C atom to make four covalent bonds, each C atom must be bonded to three H atoms. The resulting molecule, whose formula is C_2H_6, is ethane:



Propane has a backbone of three C atoms surrounded by H atoms. You should be able to verify that the molecular formula for propane is C_3H_8:



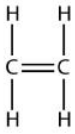
The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule. For example, the condensed structural formula for ethane is CH_3CH_3, while for propane it is $CH_3CH_2CH_3$. Table 11.1.1 - The First 10 Alkanes, gives the molecular formulas, the condensed structural formulas, and the names of the first 10 alkanes.

Table 11.1.1 The First 10 Alkanes

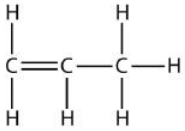
Molecular Formula	Condensed Structural Formula	Name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane

Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Alkenes have a C–C double bond. Because they have less than the maximum number of H atoms possible, they are **unsaturated hydrocarbons**. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:

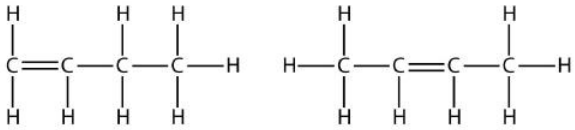


The next largest alkene—propene—has three C atoms with a C–C double bond between two of the C atoms. It is also known as propylene:



What do you notice about the names of alkanes and alkenes? The names of alkenes are the same as their corresponding alkanes except that the ending is *-ene*, rather than *-ane*. Using a stem to indicate the number of C atoms in a molecule and an ending to represent the type of organic compound is common in organic chemistry, as we shall see.

With the introduction of the next alkene, butene, we begin to see a major issue with organic molecules: choices. With four C atoms, the C–C double bond can go between the first and second C atoms or between the second and third C atoms:



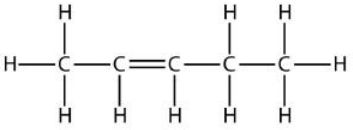
2 structural formulas for butene, with the first butene having the double bond on the first and second carbon from the left and the latter having its double bond on the second and third carbon from the left.

(A double bond between the third and fourth C atoms is the same as having it between the first and second C atoms, only flipped over.) The rules of naming in organic chemistry require that these two substances have different names. The first molecule is named *1-butene*, while the second molecule is named *2-butene*. The number at the beginning of the name indicates where the double bond originates. The lowest possible number is used to number a feature in a molecule; hence, calling the second molecule 3-butene would be incorrect. Numbers are common parts of organic chemical names because they indicate which C atom in a chain contains a distinguishing feature.

The compounds 1-butene and 2-butene have different physical and chemical properties, even though they have the same molecular formula—C_4H_8. Different molecules with the same molecular formula are called **isomers**. Isomers are common in organic chemistry and contribute to its complexity.

Example 11.1.1

Based on the names for the butene molecules, propose a name for this molecule.



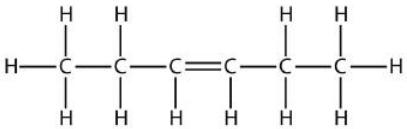
A structural formula of a five carbon molecule with a double bond on the third and fourth carbon from the left. There are ten hydrogen atoms in total.

Solution

With five C atoms, we will use the *pent-* stem, and with a C–C double bond, this is an alkene, so this molecule is a pentene. In numbering the C atoms, we use the number *2* because it is the lower possible label. So this molecule is named 2-pentene.

Exercise 11.1.1

Based on the names for the butene molecules, propose a name for this molecule.



A structural formula of a six carbon molecule with a double bond on the third and fourth carbon from the left. There are twelve hydrogen atoms in total.

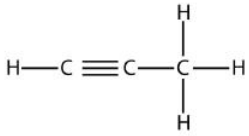
Answer

3-hexene

Alkynes, with a C–C triple bond, are named similarly to alkenes except their names end in *-yne*. The smallest alkyne is ethyne, which is also known as acetylene:

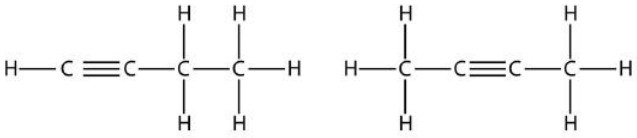


Propyne has the structure



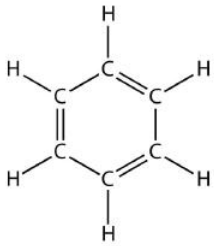
Structural formula showing three carbon molecules with a triple bond present between the first and second carbon atom. The appropriate number of hydrogen atoms is attached to each carbon atom.

With butyne, we need to start numbering the position of the triple bond, just as we did with alkenes:



Two structural formula of butyne. One butyne has a triple bond between the first and second carbon atom, while two butyne has the triple bond between the second and third carbon atom.

Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



The six carbons are arranged in a hexagon pattern with one hydrogen atom emerging outwards from each carbon atom. The presence of a double bond is alternated between every other carbon atom.

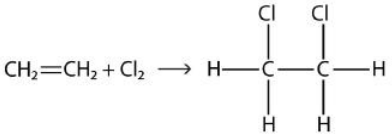
The alternating single and double C–C bonds give the benzene ring a special stability, and it does not react like an alkene as might be suspected. Benzene has the molecular formula C_6H_6; in larger aromatic compounds, a different atom replaces one or more of the H atoms.

As fundamental as hydrocarbons are to organic chemistry, their properties and chemical reactions are rather mundane. Most hydrocarbons are nonpolar because of the close electronegativities of the C and H atoms. As such, they dissolve only sparingly in H_2O and other polar solvents. Small hydrocarbons, such as methane and ethane, are gases at room temperature, while larger hydrocarbons, such as hexane and octane, are liquids. Even larger hydrocarbons are solids at room temperature and have a soft, waxy consistency.

Hydrocarbons are rather unreactive, but they do participate in some classic chemical reactions. One common reaction is substitution with a halogen atom by combining a hydrocarbon with an elemental halogen. Light is sometimes used to promote the reaction, such as this one between methane and chlorine:

$$CH_4 + Cl_2 \overset{light}{\rightarrow} CH_3Cl + HCl$$

Halogens can also react with alkenes and alkynes, but the reaction is different. In these cases, the halogen reacts with the C–C double or triple bond and inserts itself onto each C atom involved in the multiple bonds. This reaction is called an **addition reaction**. One example is



Structural formula showing the reaction of ethylene with a chlorine molecule to form ethylene dichloride.

The reaction conditions are usually mild; in many cases, the halogen reacts spontaneously with an alkene or an alkyne.

Hydrogen can also be added across a multiple bond; this reaction is called a **hydrogenation reaction**. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed at a reasonable pace:

$$CH_2 = CH_2 + H_2 \overset{metal\ catalyst}{\rightarrow} CH_3CH_3$$

By far the most common reaction of hydrocarbons is **combustion**, which is the combination of a hydrocarbon with O_2 to make CO_2 and H_2O. The combustion of hydrocarbons is accompanied by a release of energy and is a primary source of energy production in our society (Figure 11.1.2 - Combustion). The combustion reaction for gasoline, for example, which can be represented by C_8H_{18}, is as follows:

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O + \sim 5060kJ$$



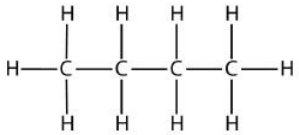
Figure 11.1.2 Combustion © Thinkstock. The combustion of hydrocarbons is a primary source of energy in our society.

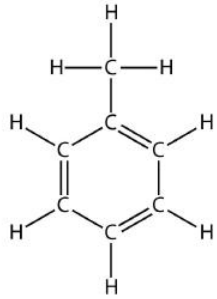
Key Takeaways

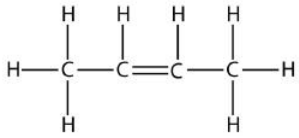
- The simplest organic compounds are hydrocarbons and are composed of carbon and hydrogen.
- Hydrocarbons can be aliphatic or aromatic; aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes.
- The combustion of hydrocarbons is a primary source of energy for our society.

Exercise 11.1.2

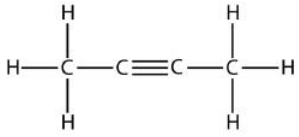
1. Define *hydrocarbon*. What are the two general types of hydrocarbons?
2. What are the three different types of aliphatic hydrocarbons? How are they defined?
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

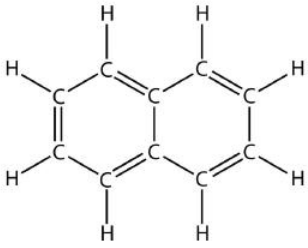
a. 

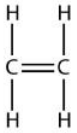
b. 

c. 

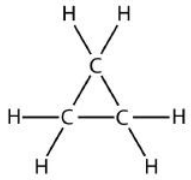
4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

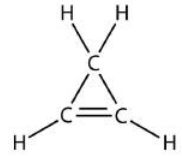
a. 

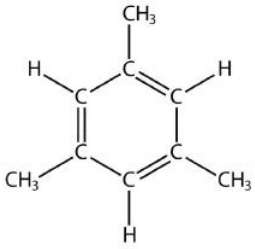
b. 

c. 

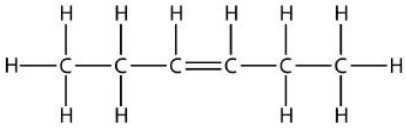
5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

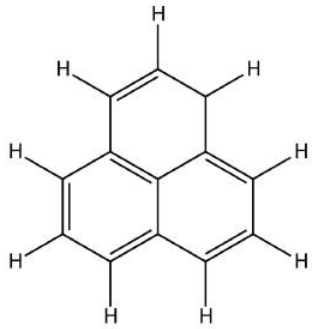
a. 

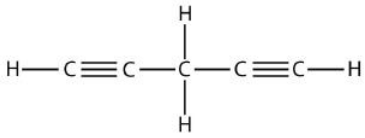
b. 

c. 

6. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

b. 

c. 

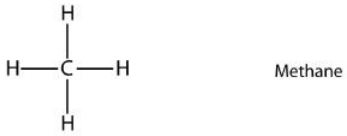
7. Name and draw the structural formulas for the four smallest alkanes.
8. Name and draw the structural formulas for the four smallest alkenes.
9. What does the term *aromatic* imply about an organic molecule?
10. What does the term *normal* imply when used for alkanes?
11. Explain why the name *1-propene* is incorrect. What is the proper name for this molecule?
12. Explain why the name *3-butene* is incorrect. What is the proper name for this molecule?
13. Name and draw the structural formula of each isomer of pentene.
14. Name and draw the structural formula of each isomer of hexyne.
15. Write a chemical equation for the reaction between methane and bromine.
16. Write a chemical equation for the reaction between ethane and chlorine.

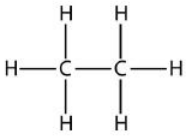
17. Draw the structure of the product of the reaction of bromine with propene.
18. Draw the structure of the product of the reaction of chlorine with 2-butene.
19. Draw the structure of the product of the reaction of hydrogen with 1-butene.
20. Draw the structure of the product of the reaction of hydrogen with 1-butene.
21. Write the balanced chemical equation for the combustion of heptane.
22. Write the balanced chemical equation for the combustion of nonane.

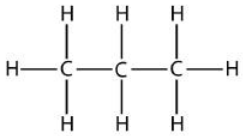
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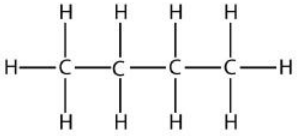
Answers

1. an organic compound composed of only carbon and hydrogen; aliphatic hydrocarbons and aromatic hydrocarbons
2.
3. a. aliphatic; alkane
   b. aromatic
   c. aliphatic; alkene
4.
5. a. aliphatic; alkane
   b. aliphatic; alkene
   c. aromatic
6.

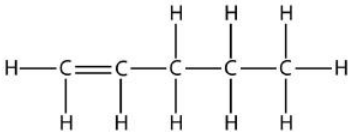

Methane


Ethane

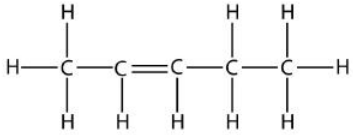

Propane


Butane

7.
8.
9. Aromatic means that the molecule has a benzene ring.
10.
11. The 1 is not necessary. The name of the compound is simply *propene*.
12.



1-Pentene



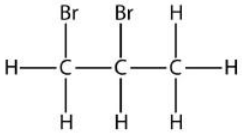
2-Pentene

13.

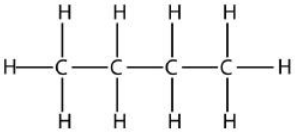
14.

15. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$

16.

17. 

18.

19. 

20.

21. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

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11.2: Branched Hydrocarbons

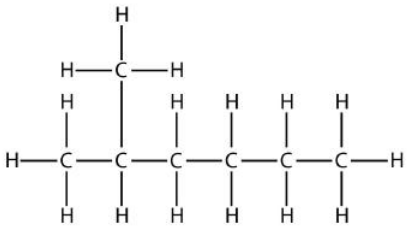
Learning Objectives

- Name a branched hydrocarbon from its structure.
- Draw the structural formula of a branched hydrocarbon from its name.

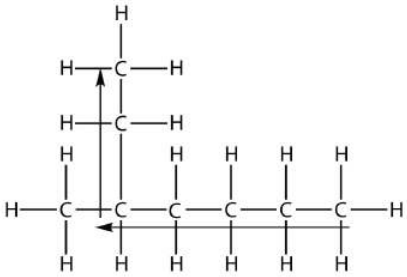
Not all hydrocarbons are straight chains. Many hydrocarbons have branches of C atoms attached to a chain. These branched alkanes are isomers of straight-chain alkanes having the same number of C atoms. However, they are different compounds with different physical and chemical properties. As such, they need different names. How do we name **branched hydrocarbons**?

There are a series of rules for naming branched alkanes (and, ultimately, for all organic compounds). These rules make up the system of **nomenclature** for naming organic molecules. Worldwide, the International Union of Pure and Applied Chemistry (IUPAC) has developed the system of nomenclature for organic compounds. So these rules are sometimes called the *IUPAC rules of nomenclature*. By learning and applying these rules, you can name any organic compound when given its structure or determine the unique structure of a molecule from its name. You have already learned the basics of nomenclature—the names of the first 10 normal hydrocarbons. Here, we will add some steps to the procedure so you can name branched hydrocarbons.

First, given the structure of an alkane, identify the longest continuous chain of C atoms. Note that the longest chain may not be drawn in a straight line. The longest chain determines the parent name of the hydrocarbon. For example, in the molecule



the longest chain of carbons has six C atoms. Therefore, it will be named as a hexane. However, in the molecule



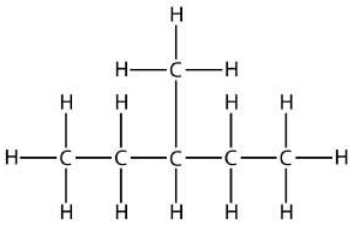
the longest chain of C atoms is not six, but seven, as shown. So this molecule will be named as a heptane.

The next step is to identify the branches, or **substituents,** on the main chain. The names of the substituents, or *alkyl groups*, are derived from the names of the parent hydrocarbons; however, rather than having the ending *-ane*, the substituent name has the ending *-yl*. Table 11.2.1 - Substituent Names, lists the substituent names for the five smallest substituents.

Table 11.2.1 Substituent Names

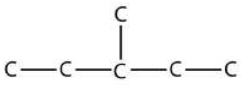
Substituent Formula	Number of C Atoms	Name of Substituent
CH_3	1	*methyl-*
CH_3CH_2	2	*ethyl-*
$CH_3CH_2CH_2$	3	*propyl-*
$CH_3CH_2CH_2CH_2$	4	*butyl-*
$CH_3CH_2CH_2CH_2CH_2$	5	*pentyl-*
and so forth	and so forth	and so forth

In naming the branched hydrocarbon, the name of the substituent is combined with the parent name of the hydrocarbon without spaces. However, there is likely one more step. The longest chain of the hydrocarbon must be numbered, and the numerical position of the substituent must be included to account for possible isomers. As with double and triple bonds, the main chain is numbered to give the substituent the lowest possible number. For example, in this alkane



the longest chain is five C atoms long, so it is a pentane. There is a one-carbon substituent on the third C atom, so there is a methyl group at position 3. We indicate the position using the number, which is followed by a hyphen, the substituent name, and the parent hydrocarbon name—in this case, 3-methylpentane. That name is specific to that particular hydrocarbon and no other molecule. Organic chemistry nomenclature is very specific!

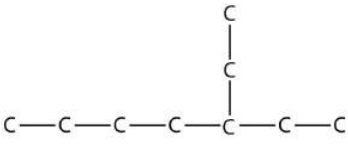
It is common to write the structural formula of a hydrocarbon without the H atoms, for clarity. So we can also represent 3-methylpentane as



where it is understood that any unwritten covalent bonds are bonds with H atoms. With this understanding, we recognize that the structural formula for 3-methylpentane refers to a molecule with the formula of C_6H_{14}.

Example 11.2.1

Name this molecule.

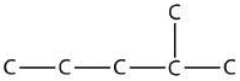


Solution

The longest continuous carbon chain has seven C atoms, so this molecule will be named as a heptane. There is a two-carbon substituent on the main chain, which is an ethyl group. To give the substituent the lowest numbering, we number the chain from the *right* side and see that the substituent is on the third C atom. So this hydrocarbon is 3-ethylheptane.

Exercise 11.2.1

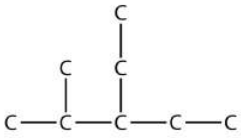
Name this molecule.



Answer

2-methylpentane

Branched hydrocarbons may have more than one substituent. If the substituents are different, then give each substituent a number (using the smallest possible numbers) and list the substituents in alphabetical order, with the numbers separated by hyphens and with no spaces in the name. So the molecule



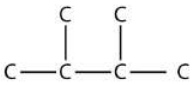
is 3-ethyl-2-methylpentane.

If the substituents are the same, then use the name of the substituent only once, but use more than one number, separated by a comma. Also, put a numerical prefix before the substituent name that indicates the number of substituents of that type. The numerical prefixes are listed in Table 11.2.2 - Numerical Prefixes to Use for Multiple Substituents. The number of the position values must agree with the numerical prefix before the substituent.

Table 11.2.2: Numerical Prefixes to Use for Multiple Substituents

Number of Same Substituent	Numerical Prefix
2	*di-*
3	*tri-*
4	*tetra-*
5	*penta-*
and so forth	and so forth

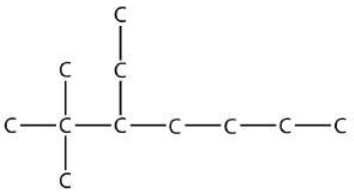
Consider this molecule:



The longest chain has four C atoms, so it is a butane. There are two substituents, each of which consists of a single C atom; they are methyl groups. The methyl groups are on the second and third C atoms in the chain (no matter which end the numbering starts from), so we would name this molecule 2,3-dimethylbutane. Note the comma between the numbers, the hyphen between the numbers and the substituent name, and the presence of the prefix *di-* before the *methyl*. Other molecules—even with larger numbers of substituents—can be named similarly.

Example 11.2.2

Name this molecule.

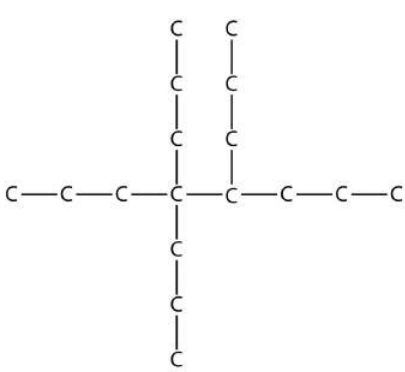


Solution

The longest chain has seven C atoms, so we name this molecule as a heptane. We find two one-carbon substituents on the second C atom and a two-carbon substituent on the third C atom. So this molecule is named 3-ethyl-2,2-dimethylheptane.

? Exercise 11.2.2

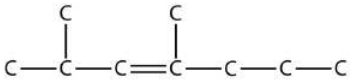
Name this molecule.



Answer

4,4,5-tripropyloctane

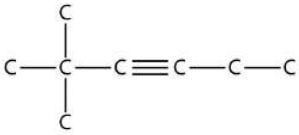
Alkenes and alkynes are named in a similar fashion. The biggest difference is that when identifying the longest carbon chain, it *must* contain the C–C double or triple bond. Furthermore, when numbering the main chain, the double or triple bond gets the lowest possible number. This means that there may be longer or higher-numbered substituents than may be allowed if the molecule were an alkane. For example, this molecule



is 2,4-dimethyl-3-heptene (note the number and the hyphens that indicate the position of the double bond).

✓ Example 11.2.3

Name this molecule.



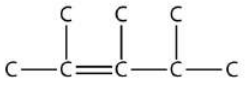
Solution

The longest chain that contains the C–C triple bond has six C atoms, so this is a hexyne molecule. The triple bond starts at the third C atom, so this is a 3-hexyne. Finally, there are two methyl groups on the chain; to give them the lowest possible number,

we number the chain from the left side, giving the methyl groups the second position. So the name of this molecule is 2,2-dimethyl-3-hexyne.

? Exercise 11.2.3

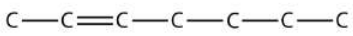
Name this molecule.



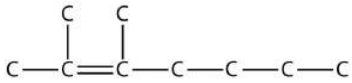
Answer

2,3,4-trimethyl-2-pentene

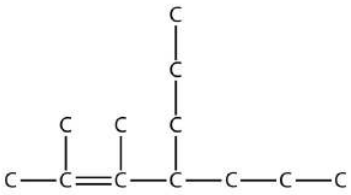
Once you master naming hydrocarbons from their given structures, it is rather easy to draw a structure from a given name. Just draw the parent chain with the correct number of C atoms (putting the double or triple bond in the right position, as necessary) and add the substituents in the proper positions. If you start by drawing the C atom backbone, you can go back and complete the structure by adding H atoms to give each C atom four covalent bonds. From the name 2,3-dimethyl-4-propyl-2-heptene, we start by drawing the seven-carbon parent chain with a double bond starting at the third carbon:



We add two one-carbon substituents to this structure on the second and third C atoms:



We finish the carbon backbone by adding a three-carbon propyl group to the fourth C atom in the parent chain:



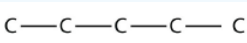
If we so choose, we can add H atoms to each C atom to give each carbon four covalent bonds, being careful to note that the C atoms in the double bond already have an additional covalent bond. (How many H atoms do you think are required? There will need to be 24 H atoms to complete the molecule.)

✓ Example 11.2.4

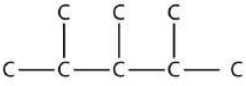
Draw the carbon backbone for 2,3,4-trimethylpentane.

Solution

First, we draw the five-carbon backbone that represents the pentane chain:



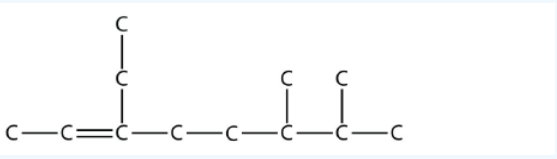
According to the name, there are three one-carbon methyl groups attached to the second, the third, and the fourth C atoms in the chain. We finish the carbon backbone by putting the three methyl groups on the pentane main chain:



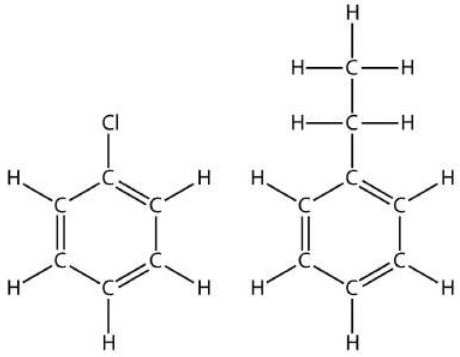
? Exercise 11.2.4

Draw the carbon backbone for 3-ethyl-6,7-dimethyl-2-octene.

Answer

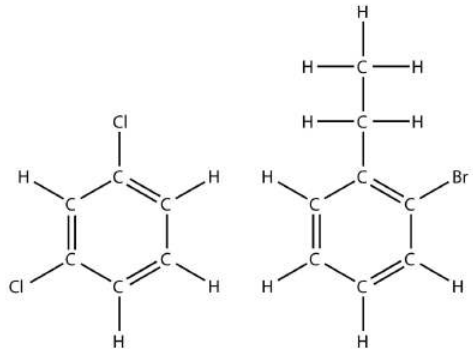


Naming substituted benzene molecules is straightforward. If there is only one substituent, the substituent is named as a side chain on a benzene molecule, like this:



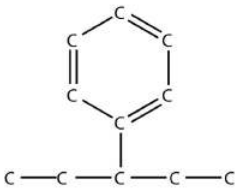
Chlorobenzene Ethylbenzene

If there are two or more substituents on a benzene molecule, the relative positions must be numbered, just as an aliphatic chain of C atoms is numbered. The substituent that is first alphabetically is assigned position 1, and the ring is numbered in a circle to give the other substituents the lowest possible number(s).



1,3-Dichlorobenzene 1-Bromo-2-ethylbenzene

If a benzene ring is treated as a substituent, it is given the name *phenyl-*. The following molecule is 3-phenylpentane:



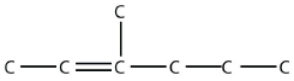
where the H atoms have been omitted for clarity.

Summary

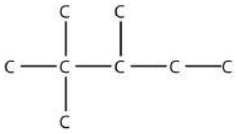
A unique name can be given to branched hydrocarbons. A unique structure can be drawn for the name of a hydrocarbon.

Exercise 11.2.5

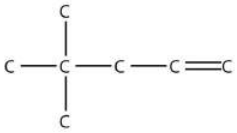
1. How does a branched hydrocarbon differ from a normal hydrocarbon?
2. How does a substituent get its unique name?
3. Name this molecule.



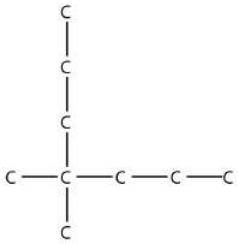
4. Name this molecule.



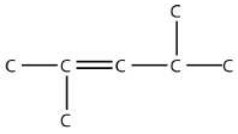
5. Name this molecule.



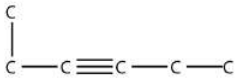
6. Name this molecule.



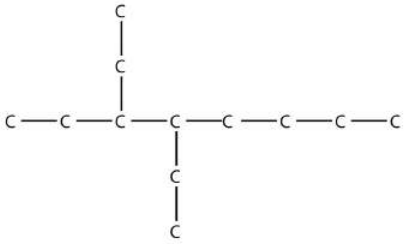
7. Name this molecule.



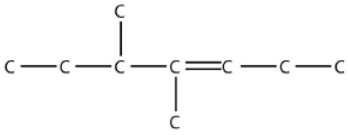
8. Name this molecule.



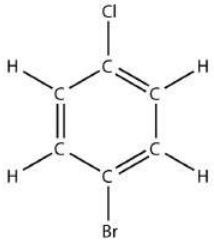
9. Name this molecule.



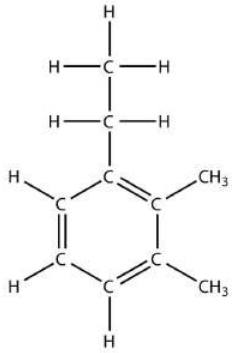
10. Name this molecule.



11. Name this molecule.



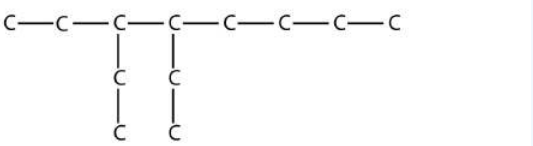
12. Name this molecule.

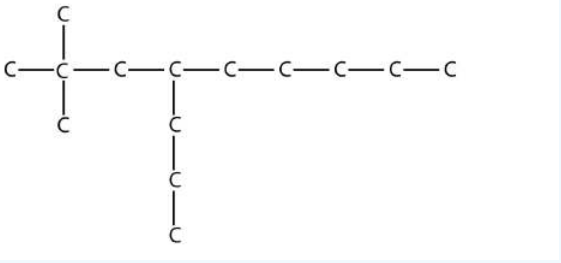


13. Draw the carbon backbone for each molecule.
    a. 3,4-diethyloctane
    b. 2,2-dimethyl-4-propylnonane
14. Draw the carbon backbone for each molecule.
    a. 3-ethyl-4-methyl-3-heptene
    b. 3,3-diethyl-1-pentyne
15. Draw the carbon backbone for each molecule.
    a. 4-ethyl-4-propyl-2-octyne
    b. 5-butyl-2,2-dimethyldecane
16. Draw the carbon backbone for each molecule.
    a. 3,4-diethyl-1-hexyne
    b. 4-propyl-3-ethyl-2-methyloctane
17. The name 2-ethylhexane is incorrect. Draw the carbon backbone and write the correct name for this molecule.
18. The name 3-butyl-7-methyloctane is incorrect. Draw the carbon backbone and write the correct name for this molecule.

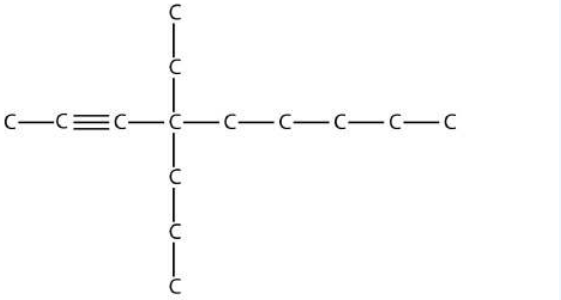
Answers

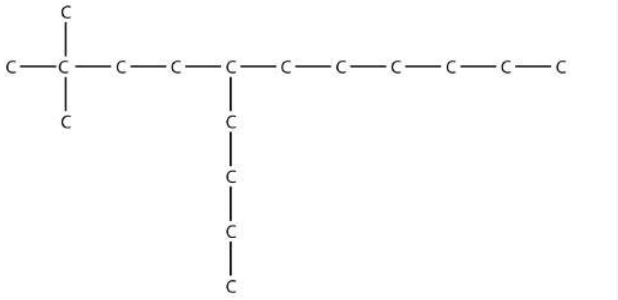
1. A branched hydrocarbon does not have all of its C atoms in a single row.
2.
3. 3-methyl-2-hexene
4.
5. 4,4-dimethyl-1-pentene
6.
7. 2,4-dimethyl-2-pentene
8.
9. 3,4-diethyloctane
10.
11. 1-bromo-4-chlorobenzene
12.

13. a. 

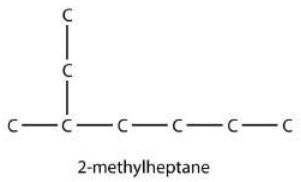
b. 

14.

15. a. 

b. 

16.

17. 

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11.3: Alkyl Halides and Alcohols

Learning Objectives

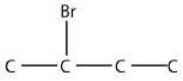
- Define *functional group*.
- Identify and name a simple alkyl halide.
- Identify and name a simple alcohol.
- Predict the product(s) of an elimination reaction of an alkyl halide or an alcohol.

A **functional group** is any collection of atoms and/or bonds with certain characteristic chemical reactions. We have already seen two functional groups: the C–C double bond and the C–C triple bond. They undergo certain characteristic chemical reactions—for example, the addition of a halogen across the multiple bond.

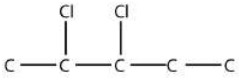
The presence of a halogen atom (F, Cl, Br, or I; also, X is used to represent any halogen atom) is one of the simplest functional groups. Organic compounds that contain a halogen atom are called **alkyl halides.** We have already seen some examples of alkyl halides when the addition of halogens across double and triple bonds was introduced in Section 16.3 - "Branched Hydrocarbons;" the products of these reactions were alkyl halides.

A simple alkyl halide can be named like an ionic salt, first by stating the name of the parent alkane as a substituent group (with the *-yl* suffix) and then the name of the halogen as if it were the anion. So CH_3Cl has the common name of methyl chloride, while CH_3CH_2Br is ethyl bromide and $CH_3CH_2CH_2I$ is propyl iodide. However, this system is not ideal for more complicated alkyl halides.

The systematic way of naming alkyl halides is to name the halogen as a substituent, just like an alkyl group, and use numbers to indicate the position of the halogen atom on the main chain. The name of the halogen as a substituent comes from the stem of the element's name plus the ending *-o*, so the substituent names are *fluoro-*, *chloro-*, *bromo-* and *iodo-*. If there is more than one of a certain halogen, we use numerical prefixes to indicate the number of each kind, just as with alkyl groups. For example, this molecule



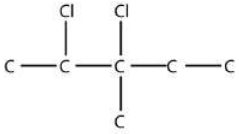
is 2-bromobutane, while this molecule



is 2,3-dichloropentane. If alkyl groups are present, the substituents are listed alphabetically. Numerical prefixes are ignored when determining the alphabetical ordering of substituent groups.

Example 11.3.1

Name this molecule.



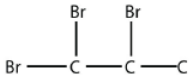
Solution

The longest carbon chain has five C atoms, so the molecule is a pentane. There are two chlorine substituents located on the second and third C atoms, with a one-carbon methyl group on the third C atom as well. The correct name for this molecule is

2,3-dichloro-3-methylpentane.

? Exercise 11.3.1

Name this molecule.



Answer

1,1,2-tribromopropane

Another simple functional group is the covalently bonded OH group. This is the **alcohol functional group**. It is not the hydroxide ion; rather than being present as a negatively charged species, in organic chemistry it is a covalently bonded functional group.

Like alkyl halides, alcohols have a common naming system and a more formal system. The common system is similar to that of alkyl halides: name the alkyl group attached to the OH group, ending with the suffix *-yl*, and add the word *alcohol* as a second word. So CH_3OH is methyl alcohol; CH_3CH_2OH is ethyl alcohol, and $CH_3CH_2CH_2OH$ is propyl alcohol.

As with alkyl halides, though, this system is limited (although for smaller alcohols, it is very common in everyday usage). The formal system of naming uses the name of the hydrocarbon containing the OH group and having the correct number of C atoms, dropping the final *-e* of the name and appending the suffix *-ol*. Thus CH_3OH is methanol and CH_3CH_2OH is ethanol. For larger alcohol molecules, we use a number to indicate the position of the OH group on the longest carbon chain, similar to the number needed for alkenes and alkynes. Again, the carbon chain is numbered to give the OH group the lowest number, no matter how large the other numbers are. So $CH_3CH_2CH_2OH$ is 1-propanol, while $CH_3CHOHCH_3$ is 2-propanol. (A common component in many medicine cabinets, 2-propanol is also known as isopropanol or isopropyl alcohol (Figure 11.3.1 - Isopropyl Alcohol).

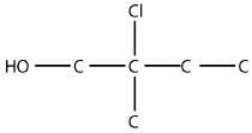


Figure 11.3.1 Isopropyl Alcohol. What you find labeled **isopropyl alcohol** in a medicine cabinet is more formally called 2-propanol.
Source: Photo courtesy of Craig Spurrier, en.Wikipedia.org/wiki/File:Rubbing.

Another acceptable way of naming an alcohol—especially a more complicated molecule—is to name the OH group as the hydroxy substituent and give it a numerical position like an alkyl group or a halogen atom. Thus, 2-propanol would be called 2-hydroxypropane by this convention.

Example 11.3.2

Name this molecule as an alcohol and as a substituted alkane.

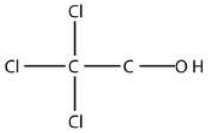


Solution

The longest carbon chain containing the OH group has four C atoms, so the parent hydrocarbon is butane. Because the OH group is on the first C atom, it is 1-butanol. There is a methyl group on the second C atom, as well as a Cl atom, so the formal name for this alcohol is 2-chloro-2-methyl-1-butanol. If naming the alcohol group as a substituent, it would be 2-chloro-1-hydroxy-2-methylbutane.

Exercise 11.3.2

Name this molecule as an alcohol and as a substituted alkane.

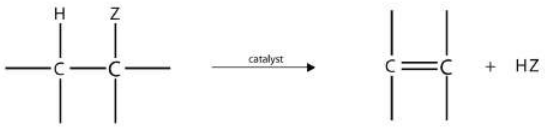


Answer

2,2,2-trichloroethanol; 2,2,2-trichloro-1-hydroxyethane

Most alkyl halides are insoluble in H_2O. Smaller alcohols, however, are very soluble in H_2O because these molecules can engage in hydrogen bonding with H_2O molecules. For larger molecules, however, the polar OH group is overwhelmed by the nonpolar alkyl part of the molecule. While methanol is soluble in H_2O in all proportions, only about 2.6 g of pentanol will dissolve in 100 g of H_2O. Larger alcohols have an even lower solubility in H_2O.

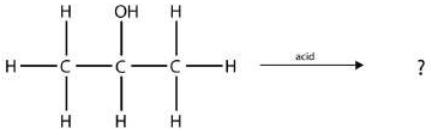
One reaction common to alcohols and alkyl halides is **elimination**, the removal of the functional group (either X or OH) and an H atom from an adjacent carbon. The general reaction can be written as follows:



where Z represents either the X or the OH group. The biggest difference between elimination in alkyl halides and elimination in alcohols is the identity of the catalyst: for alkyl halides, the catalyst is a strong base; for alcohols, the catalyst is a strong acid. For compounds in which there are H atoms on more than one adjacent carbon, a mixture of products results.

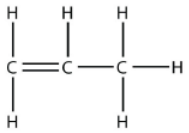
Example 11.3.3

Predict the organic product(s) of this reaction.



Solution

Under these conditions, an HOH (otherwise known as H_2O) molecule will be eliminated, and an alkene will be formed. It does not matter which adjacent carbon loses the H atom; in either case the product will be

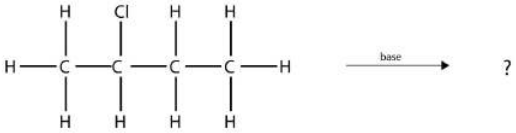


which is propene.

Exercise 11.3.3

Predict the organic product(s) of this reaction.

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Answer

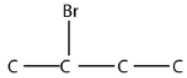
1-butene and 2-butene

Key Takeaways

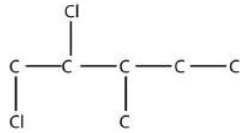
- Alkyl halides have a halogen atom as a functional group.
- Alcohols have an OH group as a functional group.
- Nomenclature rules allow us to name alkyl halides and alcohols.
- In an elimination reaction, a double bond is formed as an HX or an HOH molecule is removed.

Exercise 11.3.4

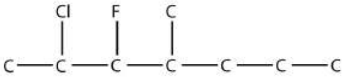
1. Define *functional group* and give two examples.
2. What is elimination? How does it differ for alkyl halides and alcohols?
3. Name this molecule.



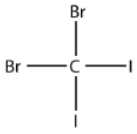
4. Name this molecule.



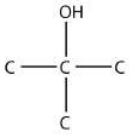
5. Name this molecule.



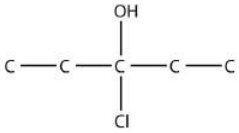
6. Name this molecule.



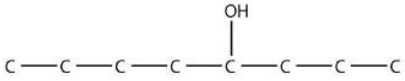
7. Name this molecule.



8. Name this molecule.

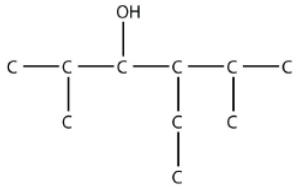


9. Name this molecule.

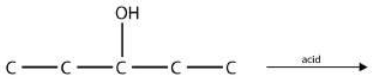


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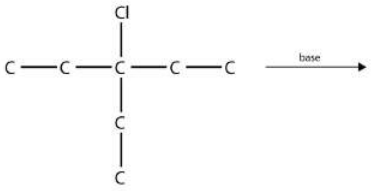
10. Name this molecule.



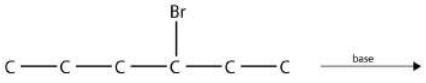
11. Predict the product(s) of this elimination reaction.



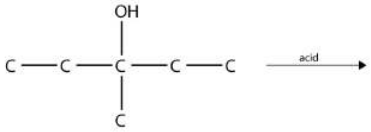
12. Predict the product(s) of this elimination reaction.



13. Predict the product(s) of this elimination reaction.



14. Predict the product(s) of this elimination reaction.



Nov 27, 2021, 11:15 AM

Answers

1. a group of atoms with a certain reactivity; halogen atoms and alcohol groups (answers will vary).
2.
3. 2-bromobutane
4.
5. 2-chloro-3-fluoro-4-methylheptane
6.
7. 2-methyl-2-propanol
8.
9. 4-octanol
10.
11. 2-pentene
12.
13. 2-hexene and 3-hexene
1.

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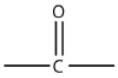
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11.4: Other Oxygen-Containing Functional Groups

Learning Objective

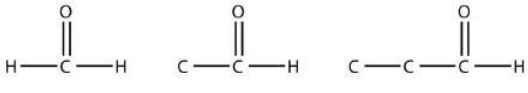
- Identify the aldehyde, ketone, acid, ester, and ether functional groups.

There are other functional groups that contain O atoms. Before we introduce them, we define the **carbonyl group**, which is formed when an O atom and a C atom are joined by a double bond:



The other two bonds on the C atom are attached to other atoms. It is the identities of these other atoms that define what specific type of compound an organic molecule is.

If one bond of the carbonyl group is made to an H atom, then the molecule is classified as an **aldehyde** (If there are two H atoms, there is only 1 C atom). When naming aldehydes, the main chain of C atoms must include the carbon in the carbonyl group, which is numbered as position 1 in the carbon chain. The parent name of the hydrocarbon is used, but the suffix *-al* is appended. (Do not confuse *-al* with *-ol*, which is the suffix used for alcohols.) So we have



Methanal has a common name with which you may be familiar: formaldehyde. The main thing to note about aldehydes is that the carbonyl group is at the *end* of a carbon chain.

A carbonyl group in the middle of a carbon chain implies that both remaining bonds of the carbonyl group are made to C atoms. This type of molecule is called a **ketone.** Despite the fact that aldehydes and ketones have the same carbonyl group, they have different chemical and physical properties and are properly grouped as two different types of compounds. The smallest ketone has three C atoms in it. When naming a ketone, we take the name of the parent hydrocarbon and change the suffix to *-one*:



The common name for propanone is acetone. With larger ketones, we must use a number to indicate the position of the carbonyl group, much like a number is used with alkenes and alkynes:



There is another way to name ketones: name the alkyl groups that are attached to the carbonyl group and add the word *ketone* to the name. So propanone can also be called dimethyl ketone, while 2-butanone is called methyl ethyl ketone.

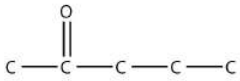
Example 11.4.1

Draw the structure of 2-pentanone.

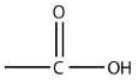
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Solution

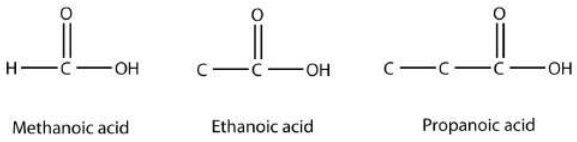
This molecule has five C atoms in a chain, with the carbonyl group on the second C atom. Its structure is as follows:



The combination of a carbonyl functional group and an OH group makes the **carboxyl group**.



Molecules with a carboxyl group are called **carboxylic acids**. As with aldehydes, the functional group in carboxylic acids is at the end of a carbon chain. Also as with aldehydes, the C atom in the functional group is counted as one of the C atoms that defines the parent hydrocarbon name. To name carboxylic acids, the parent name of the hydrocarbon is used, but the suffix *-oic acid* is added:



Methanoic acid and ethanoic acid are also called formic acid and acetic acid, respectively. Formic acid is the compound that makes certain ant bites sting, while acetic acid is the active substance in vinegar.

How acidic are carboxylic acids? It turns out that they are not very acidic. No carboxylic acid is on the list of strong acids (Table 11.4.1). This means that all carboxylic acids are weak acids. A 1 M solution of formic acid is only about 1.3% dissociated into H^+ ions and formate ions, while a similar solution of acetic acid is ionized by about only 0.4%. Some carboxylic acids are stronger—for example, trichloroacetic acid is about 45% dissociated in aqueous solution. But no carboxylic acid approaches the 100% dissociation amount required by the definition of a strong acid.

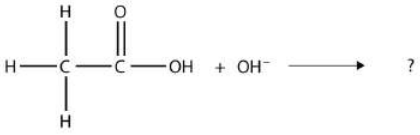
As their name suggests, however, carboxylic acids do act like acids in the presence of bases. The H atom in the carboxyl group comes off as the H^+ ion, leaving a **carboxylate anion**:



Carboxylate ions are named from the acid name: the *-oic acid* is replaced with *-oate* to name the ion.

Example 11.4.2:

Complete the chemical reaction. Can you name the carboxylate ion formed?



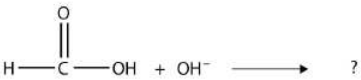
Solution

The OH^- ion removes the H atom that is part of the carboxyl group:

The carboxylate ion, which has the condensed structural formula $CH_3CO_2^-$, is the ethanoate ion, but it is commonly called the acetate ion.

Exercise 11.4.1

Complete the chemical reaction. Can you name the carboxylate ion formed?

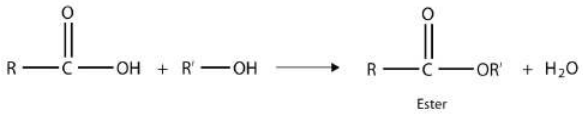


Answer



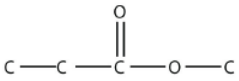
The anion is the methanoate ion, which is commonly called the formate ion.

One reaction to consider is that of a carboxylic acid and an alcohol. When combined under the proper conditions, a water molecule will be removed, and the remaining pieces will combine to form a new functional group—the **ester** functional group:



Ester

Note how the acid molecule contributes one alkyl side (represented by R), while the alcohol contributes the other side (represented by R′). Esters are named using the alkyl group name from the alcohol plus the carboxylate name from the acid. For example, the molecule



is called methyl propanoate.

Chemistry is Everywhere: Esters, Fragrances, and Flavorings

Esters are very interesting compounds, in part because many have very pleasant odors and flavors. (Remember, never taste anything in the chemistry lab!) Many esters occur naturally and contribute to the odor of flowers and the taste of fruits. Other esters are synthesized industrially and are added to food products to improve their smell or taste; it is likely that if you eat a product whose ingredients include artificial flavorings, those flavorings are esters. Here are some esters and their uses, thanks to their odors, flavors, or both:

Table with four columns and seven rows. The first column on the left is labeled Ester and underneath in the rows has different esters. The second column is labeled Tastes/Smells Like and underneath in the rows has different tastes and smells. The third column is labeled Ester and underneath in the rows has different esters. The last and fourth column is labeled Tastes/Smells Like and underneath in the rows has different tastes and smells.

Ester	Tastes/Smells Like	Ester	Tastes/Smells Like
allyl hexanoate	pineapple	isobutyl formate	raspberry
benzyl acetate	pear	isobutyl acetate	pear
butyl butanoate	pineapple	methyl phenylacetate	honey
ethyl butanoate	banana	nonyl caprylate	orange
ethyl hexanoate	pineapple	pentyl acetate	apple
ethyl heptanoate	apricot	propyl ethanoate	pear
ethyl pentanoate	apple	propyl isobutyrate	rum

Finally, the **ether** functional group is an O atom that is bonded to two organic groups: R-O-R′

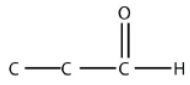
The two R groups may be the same or different. Naming ethers is like the alternate way of naming ketones. In this case, the R groups are named sequentially, and the word *ether* is appended. The molecule CH_3OCH_3 is dimethyl ether, while $CH_3OCH_2CH_3$ is methyl ethyl ether. Diethyl ether, another ether, was once used as an anesthetic, but its flammability and toxicity caused it to fall out of favor. Smaller ether molecules that are liquids at room temperature are common solvents for organic chemical reactions.

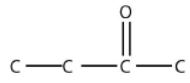
Key Takeaway

- Aldehydes, ketones, carboxylic acids, esters, and ethers have oxygen-containing functional groups.

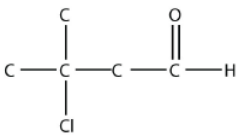
Exercise 11.4.2

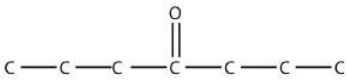
1. Name a similarity between the functional groups found in aldehydes and ketones. Can you name a difference between them?
2. Explain how a carboxylic acid is used to make an ester.
3. Name each molecule.

a. 

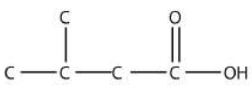
b. 

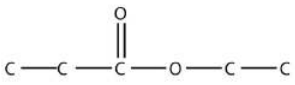
4. Name each molecule.

a. 

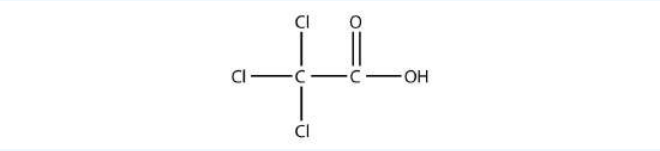
b. 

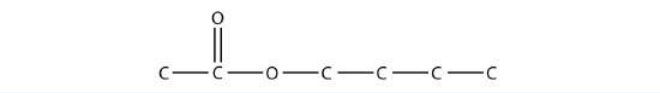
5. Name each molecule.

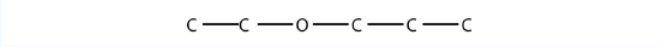
a. 

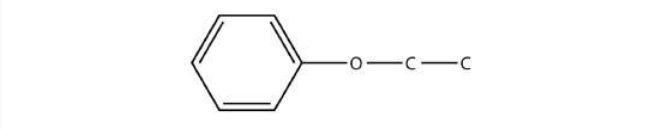
b. 

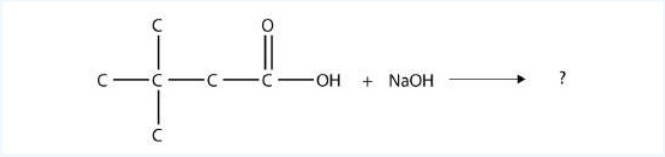
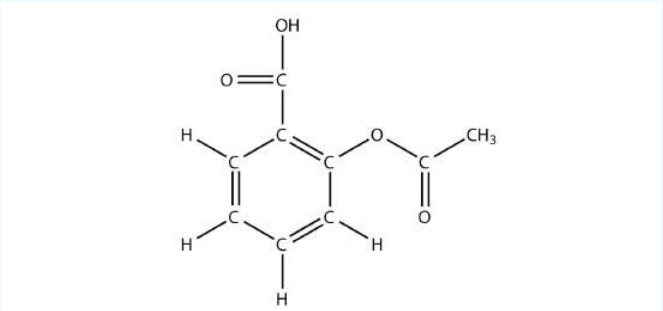
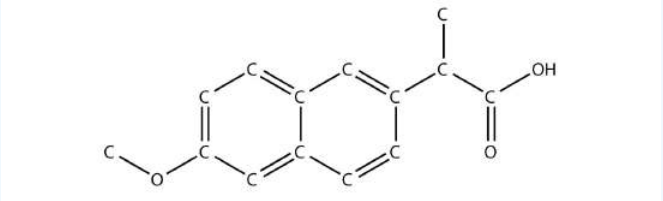
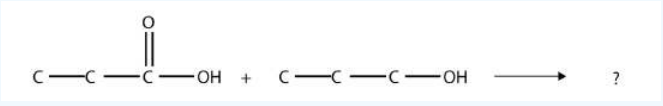
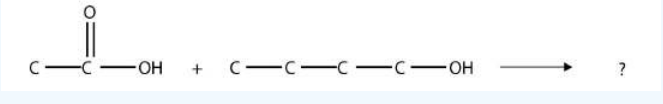
6. Name each molecule.

a. 

b. 

7. Name the molecule. 

8. Name the molecule. 

9. Give an alternate but acceptable name to the molecule in Exercise 3b.
10. Give an alternate but acceptable name to the molecule in Exercise 4b.
11. Complete this chemical reaction. Propanoic acid reacts with <span class=KOH." style="width: 550px; height: 82px;" width="550px" height="82px" data-cke-saved-src="/@api/deki/files/96632/Ex_11.png" src="/@api/deki/files/96632/Ex_11.png" data-quail-id="209">
12. Complete this chemical reaction. 
13. The drug known as aspirin has this molecular structure:  Identify the functional group(s) in this molecule.
14. The drug known as naproxen sodium is the sodium salt of this molecule:  (The extra H atoms are omitted for clarity.) Identify the functional group(s) in this molecule.
15. Identify the ester made by reacting these molecules. 
16. Identify the ester made by reacting these molecules. 

Nov 27, 2021, 2:06 PM

Answers

1. They both have a carbonyl group, but an aldehyde has the carbonyl group at the end of a carbon chain, and a ketone has the carbonyl group in the middle.
2.
3. a. propanal
   b. 2-butanone
4.
5. a. 3-methylbutanoic acid
   b. ethyl propionate
6.
7. ethyl propyl ether
8.
9. ethyl methyl ketone
10.
11. $H_2O + KCH_3CH_2CO_2$
12.
13. acid, ester, and aromatic (benzene ring)
14.
15. propyl propionate

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11.5: Other Nitrogen and Sulfur-Containing Functional Groups

Learning Objective

- Identify the amine, amide, and thiol functional groups.

There are some common and important functional groups that contain elements other than oxygen. In this section, we will consider three of them.

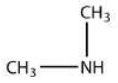
Nitrogen-Containing Compounds

An **amine** is an organic derivative of ammonia (NH_3). In amines, one or more of the H atoms in NH_3 is substituted with an organic group. A *primary* amine has one H atom substituted with an R group:



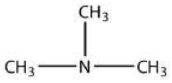
Methylamine

A *secondary* amine has two H atoms substituted with R groups:



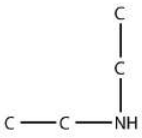
Dimethylamine

A *tertiary* amine has all three H atoms substituted with R groups:

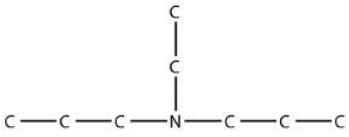


Trimethylamine

Naming simple amines is straightforward: name the R groups as substituents and then add the suffix *-amine*, using numerical suffixes on the substituent names as necessary. This amine



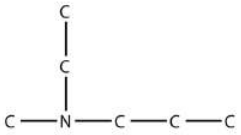
is diethylamine (the H atoms on the C atoms are omitted for clarity), while this amine



is ethyldipropylamine.

Example 11.5.1

Name this amine.

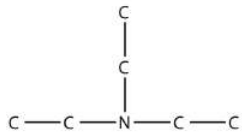


Solution

This amine has a methyl group, an ethyl group, and a propyl group. Listing the names in alphabetical order, this amine is ethylmethylpropylamine.

? Exercise 11.5.1

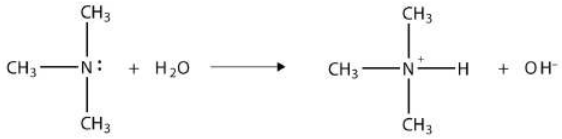
Name this amine.



Answer

triethylamine

As with NH_3, the N atom in amines can accept a proton onto the lone electron pair on the N atom. That is, amines act as Brønsted-Lowry bases (i.e., proton acceptors):



The amine becomes an ion, the organic counterpart of the ammonium (NH_4^+) ion.

All amines are weak bases. The weakness of amines is about the same as that of carboxylic acids. N-containing organic compounds are very common in nature, and they all act as weak bases. Some of these compounds have rather complicated structures. Figure 11.5.1 - Some Naturally Occurring N-Containing Compounds, shows some N-containing substances that you may recognize.

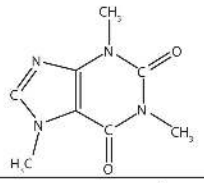
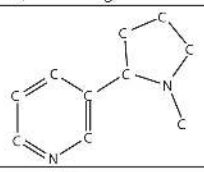
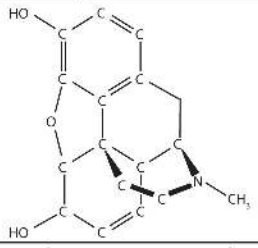
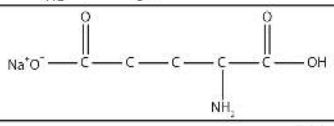
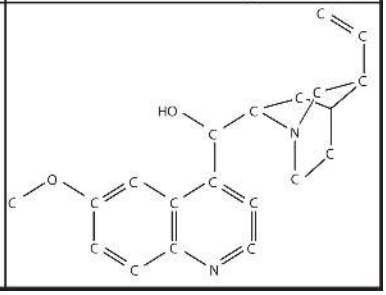
Compound	Structure — Atoms not shown are assumed to be H atoms, which are omitted for clarity
Caffeine (stimulant found in teas and coffees)	
Nicotine (addictive compound found in tobacco)	
Morphine (painkiller)	
Monosodium glutamate (food additive and flavor enhancer)	
Quinine (antimalaria compound found in the bark of the cinchona tree)	

Figure 11.5.1 Some Naturally Occurring N-Containing Compounds.

Nitrogen-containing compounds occur frequently in nature. Here are some that you might encounter in the course of your everyday life.

An **amide** functional group is a combination of an amine group and a carbonyl group:



Amide

Amides are actually formed by bringing together an amine-containing molecule and a carboxylic acid-containing molecule. A molecule of H_2O is lost, much like when an ester forms:



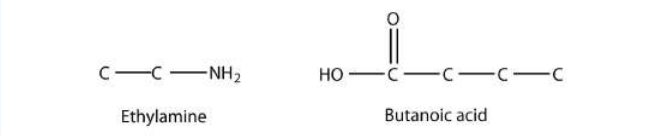
The bond between the N of the amine group and the C of the carbonyl group is called an **amide bond.** Amide bonds are particularly important in biological molecules called proteins, which are composed of strings of amino acids—molecules that have an amine group and a carboxylic acid group within them. The amine group on one amino acid reacts with the carboxylic acid group of another amino acid, making a chain held together by amide bonds. We will consider proteins later in this chapter.

Example 11.5.2

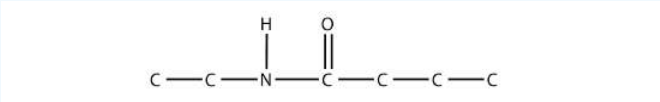
Draw the structure of the amide formed by the combination of ethylamine and butanoic acid.

Solution

The structures of ethylamine and butanoic acid are as follows:



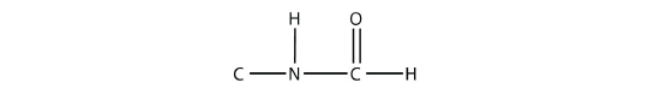
When they come together to make an amide, an H_2O molecule is lost, and the N of the amine group bonds to the C of the carboxyl group. The resulting molecule is as follows:



Exercise 11.5.2

Draw the structure of the amide formed by the combination of methylamine and formic acid.

Answer

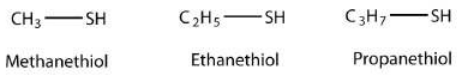


Sulfur-Containing Compounds

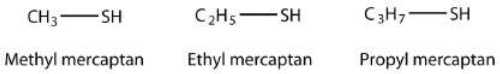
Sulfur is below oxygen on the periodic table, and it occasionally shows some similar chemistry. One similarity is that an S atom can take the place of an O atom in an alcohol, to make a molecule that looks like this:

R-SH

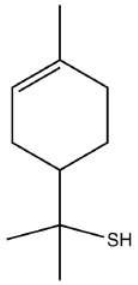
The sulfur analog of an alcohol is called a **thiol**. The formal way of naming a thiol is similar to that of alcohols, except that instead of using the *suffix-ol*, you use *-thiol* as the suffix. The following illustrates *thiol* nomenclature:



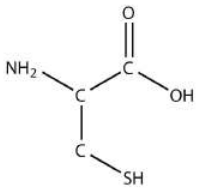
An older system uses the word *mercaptan* in naming simple thiols, much like the word *alcohol* is used with small alcohols. These thiols can also be named like this:



Many thiols have strong, objectionable odors; indeed, the spray from skunks is composed of thiols and is detectable by the human nose at concentrations less than 10 ppb. Because natural gas is odorless, thiols are intentionally added to natural gas—at very low levels, of course—so that gas leaks can be more easily detected. Not all thiols have objectionable odors; this thiol is responsible for the odor of grapefruit:



One amino acid that is a thiol is cysteine:



Cysteine plays an important role in protein structure. If two cysteine amino acids in a protein chain approach each other, they can be oxidized, and a S–S bond (also known as a *disulfide bond*) is formed:

$$\text{R–SH + HS–R} \rightarrow \text{R–S–S–R}$$

where the R group is the rest of the cysteine molecule. The disulfide bond is strong enough to fix the position of the two cysteine groups, thus imposing a structure on the protein. Hair is composed of about 5% cysteine, and the breaking and remaking of disulfide bonds between cysteine units is the primary mechanism behind straightening and curling hair (hair "perms").

Food and Drink Application: Amino Acids, Essential and Otherwise

The text mentioned cysteine, an amino acid. Amino acids are the fundamental building blocks of proteins, a major biological component. Proteins are a necessary part of the diet; meat, eggs, and certain plant foods such as beans and soy are good sources of protein and amino acids.

All life on Earth—from the lowliest single-celled organism to humans to blue whales—relies on proteins for life, so all life on Earth is dependent on amino acids. The human body contains 20 different amino acids (curiously, other organisms may have a different number of amino acids). However, not all of them must be obtained from the diet. The body can synthesize 12 amino acids. The other 8 *must* be obtained from the diet. These 8 amino acids are called the *essential amino acids*. Daily requirements range from 4 mg per kilogram of body weight for tryptophan to 40 mg per kilogram of body weight for leucine. Infants and children need a greater mass per kg of body weight to support their growing bodies; also, the number of amino acids that are considered essential for infants and children is greater than for adults due to the greater protein synthesis associated with growth.

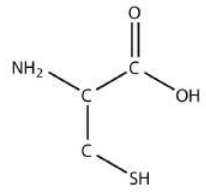
Because of the existence of essential amino acids, a diet that is properly balanced in protein is necessary. Rice and beans, a very popular food dish in Latin cuisines, actually provides all of the essential amino acids in one dish; without one component, the dish would be nutritionally incomplete. Corn (maize) is the most-grown grain crop in the world, but an over-reliance on it as a primary food source deprives people of lysine and tryptophan, which are two essential amino acids. (Indeed, it is now widely accepted that the disappearance of certain native American groups was largely due to the overuse of corn as the staple food.) People on restricted diets, whether out of necessity or by choice (e.g., vegetarians), may be missing the proper amount of an essential amino acid. It is important to vary the diet when possible to ensure ingestion of a wide range of protein sources.

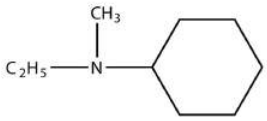
Key Takeaway

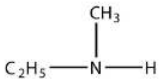
- Other functional groups include amine, amide, and thiol functional groups.

Exercise 11.5.3

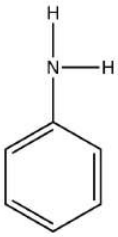
1. What are the structure and name of the smallest amine?
2. What are the structure and name of the smallest thiol?
3. Identify each compound as a primary, secondary, or tertiary amine.

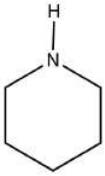
a. 

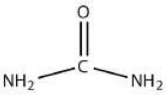
b. 

c. 

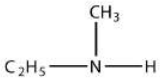
4. Identify each compound as a primary, secondary, or tertiary amine.

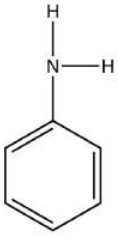
a. 

b. 

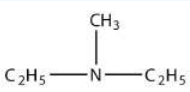
c. 

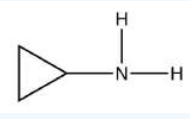
5. Write the chemical reaction between each amine in Exercise 3 and HCl.
6. Write the chemical reaction between each amine in Exercise 4 and HNO_3.
7. Name each amine.

a. 

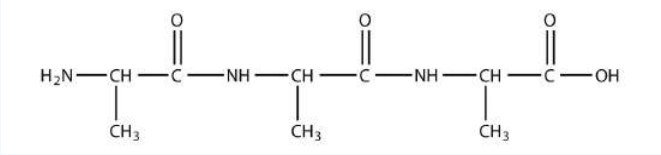
b. 

8. Name each amine.

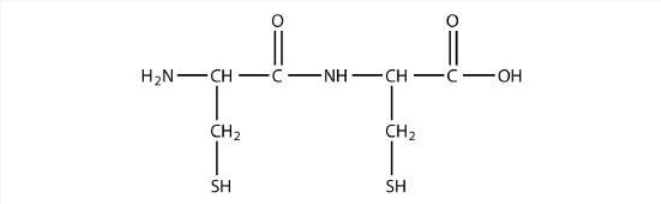
a. 

b. 

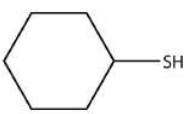
9. A *peptide* is a short chain of amino acids connected by amide bonds. How many amide bonds are present in this peptide?



10. How many amide bonds are present in this peptide? (See Exercise 9 for the definition of a peptide.)



11. Draw the backbone structure of the amide formed by reacting propylamine with propanoic acid.
12. Draw the backbone structure of the amide formed by reacting hexylamine with ethanoic acid.
13. Name each thiol using the *-thiol* suffix.

a. 

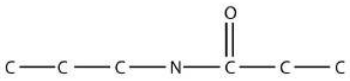
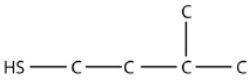
b. $C_4H_9–SH$

14. Name each thiol in Exercise 13 with the mercaptan label.
15. One component of skunk spray is 3-methyl-1-butanethiol. Draw its structure. (The 1 indicates the position of the S atom.)
16. An S–S bond can be fairly easily broken into proteins, yielding two lone cysteine units in a protein chain. Is this process an oxidation or a reduction? Explain your answer.

Nov 27, 2021, 10:50 AM

Answers

1. CH_3NH_2; methylamine
2.
3. a. primary
   b. tertiary
   c. secondary
4.
5. a. $C_3H_3CO_2HSHNH_2 + HCl \rightarrow C_3H_3CO_2HSHNH_3Cl$
   b. $(C_6H_{11})(C_2H_5)(CH_3)N + HCl \rightarrow (C_6H_{11})(C_2H_5)(CH_3)NHCl$
   c. $(C_2H_5)(CH_3)NH + HCl \rightarrow (C_2H_5)(CH_3)NH_2Cl$
6.
7. a. ethylmethylamine
   b. phenylamine
8.

9. two
10.
11. 
12.
13. a. cyclohexanethiol
    b. butanethiol
14.
15. 

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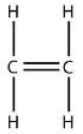
- **16.6: Other Functional Groups** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/beginning-chemistry.

11.6: Polymers

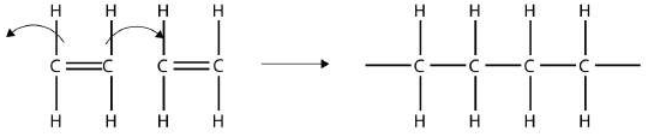
Learning Objectives

- Define the terms *monomer* and *polymer*.
- Draw the structure of a polymer from its monomer.

Among other applications, organic chemistry has had a huge impact on the development of modern materials called polymers. Many objects in daily life are composed of polymers; curiously, so are several important biological materials. Consider a molecule with a double bond, such as ethylene:

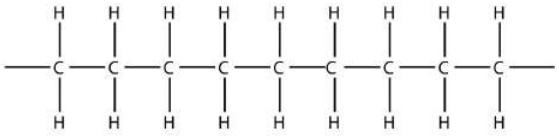


Imagine the bond between the carbons opening up and attacking another ethylene molecule:



The double bond between the two carbons is depicted with electron pushing arrows attacking another ethylene.

Now imagine further that the second ethylene molecule's double bond opens up and attacks a third ethylene molecule, which also opens up its double bond and attacks a fourth ethylene molecule, and so forth. The end result is a long, virtually endless molecule:



This long, almost nonstop molecule is called a **polymer** (from the Greek meaning "many parts"). The original part, ethylene, is called the **monomer** (meaning "one part"). The process of making a polymer is called **polymerization**. A polymer is an example of a *macromolecule*, the name given to a large molecule.

Simple polymers are named after their monomers. The ethylene polymer is formally called poly(ethylene), although in common use, the names are used without parentheses: polyethylene. Because adding one monomer to another forms this polymer, polyethylene is an example of a type of polymer called *addition polymers*. Figure 11.6.1 - Some Monomers and Their Addition Polymers, lists some addition polymers and their monomers. One of them, poly(ethylene oxide), results not from the opening of a double bond but the opening of a ring in the monomer; the concept of bonding with other monomers, however, is the same.

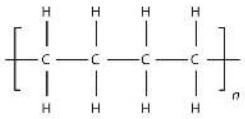
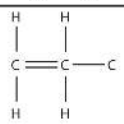
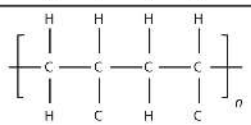
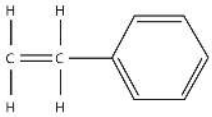
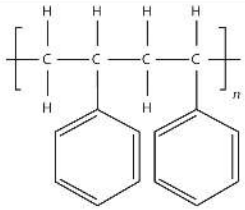
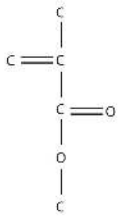
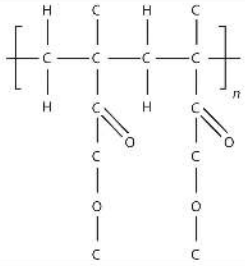
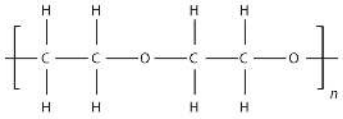
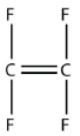
Monomer	Monomer Name	Polymer	Polymer Name
	ethylene		poly(ethylene)
	propylene		poly(propylene)
	styrene		poly(styrene)
	methyl methacrylate		poly(methyl methacrylate)
	ethylene oxide		poly(ethylene oxide)

Figure 11.6.1: Some Monomers and Their Addition Polymers

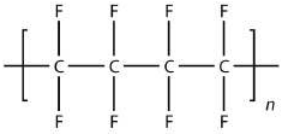
Example 11.6.1

Draw the polymer that results from the polymerization of tetrafluoroethylene.



Solution

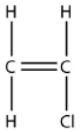
In the case of this monomer, the double bond opens up and joins to other monomers, just as with ethylene. The polymer that is made has this structure:



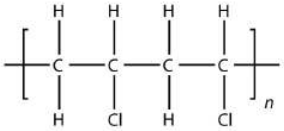
Exercise 11.6.1

Draw the polymer that results from the polymerization of vinyl chloride.

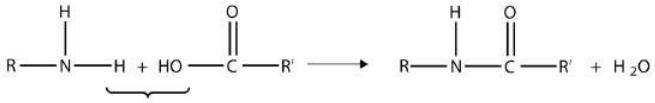
https://chem.libretexts.org/@go/page/469502



Answer

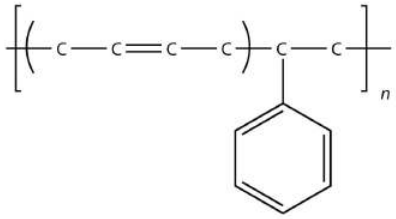


Another type of polymer is the *condensation polymer*, which is a polymer made when two different monomers react together and release some other small molecule as a product. We have already seen an example of this, in the formation of an amide bond:



Here, H_2O is released when the ends of the molecules react to form a polymer.

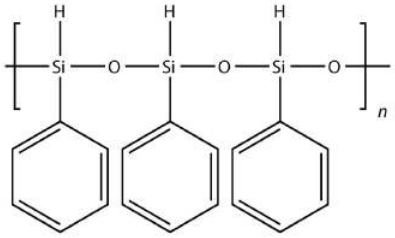
Related to condensation polymers are the *copolymers*, polymers made from more than one type of monomer. For example, ethylene and propylene can be combined into a polymer that is a mixture of the two monomers. A common form of synthetic rubber called styrene butadiene rubber (SBR) is made from two monomers: styrene and butadiene:



The physical and chemical properties of polymers vary widely, based on their monomers, structures, and additives. Among the other properties that can be modified based on these factors include: solubility in H_2O and other solvents, melting point, flammability, color, hardness, transparency, film thickness, wet-ability, surface friction, mold-ability, particle size...the list goes on.

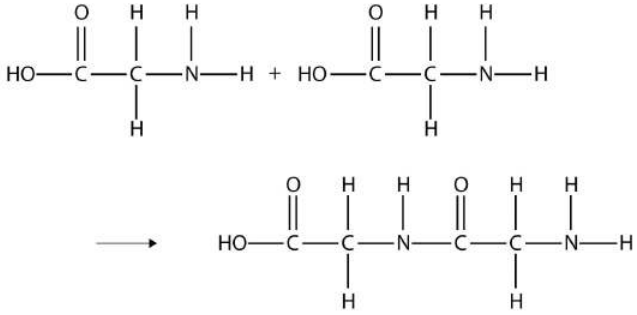
The uses of polymers are almost too numerous to consider. Anything that you might describe as "plastic" is likely a polymer. Polymers are used to make everything from toothbrushes to computer cases to automobile parts. Many epoxy-based adhesives are condensation polymers that adhere strongly to other surfaces. Polyurethane paints and coatings are polymers, as are the polyester fabrics used to make clothing. Nylon, Dacron, and Mylar are polymers (in fact, both Dacron and Mylar are forms of polyethylene terephthalate [PET]). The product known as Saran Wrap was originally constructed from Saran, a name for poly(vinylidene chloride), which was relatively impervious to oxygen and could be used as a barrier to help keep food fresh. (It has since been replaced with polyethylene, which is not as impervious to atmospheric oxygen.) Poly(vinyl chloride) is the third-most produced polymer [after poly(ethylene) and poly(propylene)] and is used to make everything from plastic tubing to automobile engine parts, water pipes to toys, flooring to waterbeds and pools.

All the polymers we have considered so far are based on a backbone of (largely) carbon. There is another class of polymers based on a backbone of Si and O atoms; these polymers are called **silicones**. The Si atoms have organic groups attached to them, so these polymers are still organic. One example of a silicone is as follows:



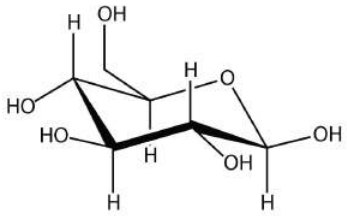
Silicones are used to make oils and lubricants; they are used as sealants for glass objects (such as aquariums) and films for waterproofing objects. Solid silicones are heat resistant and rubbery and are used to make cookware and electrical insulation.

Some very important biological materials are polymers. Of the three major food groups, polymers are represented in two: proteins and carbohydrates. Proteins are polymers of amino acids, which are monomers that have an amine functional group and a carboxylic acid functional group. These two groups react to make a condensation polymer, forming an amide bond:

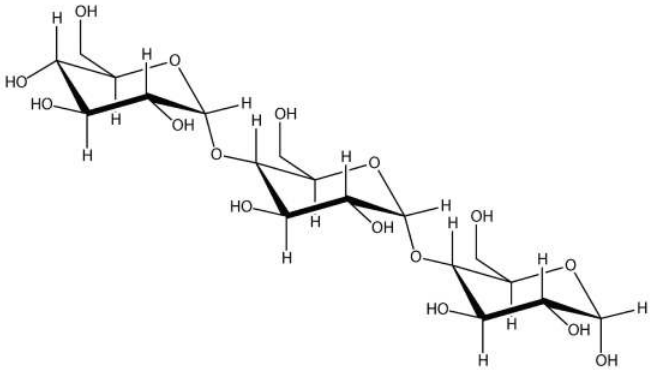


Proteins are formed when hundreds or even thousands of amino acids form amide bonds to make polymers. Proteins play a crucial role in living organisms.

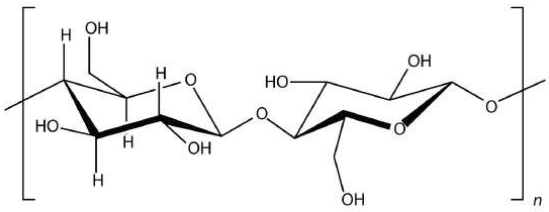
A *carbohydrate* is a compound that has the general formula $C_n(H_2O)_n$. Many carbohydrates are relatively small molecules, such as glucose:



Linking hundreds of glucose molecules together makes a relatively common material known as *starch*:



Starch is an important source of energy in the human diet. Note how individual glucose units are joined together. They can also be joined together in another way, like this:



This polymer is known as *cellulose*. Cellulose is a major component in the cell walls of plants. Curiously, despite the similarity in the building blocks, some animals (such as humans) cannot digest cellulose; those animals that can digest cellulose typically rely on symbiotic bacteria in the digestive tract for the actual digestion. Animals do not have the proper enzymes to break apart the glucose units in cellulose, so it passes through the digestive tract and is considered *dietary fiber*.

DNA

Deoxyribonucleic acid (*DNA*) and *ribonucleic acid* (*RNA*) are also polymers, composed of long, three-part chains consisting of phosphate groups, sugars with 5 C atoms (ribose or deoxyribose), and N-containing rings referred to as bases. Each combination of the three parts is called a nucleotide; DNA and RNA are essentially polymers of nucleotides that have rather complicated, but intriguing structures (Figure 11.6.2). DNA is the fundamental material in chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis.

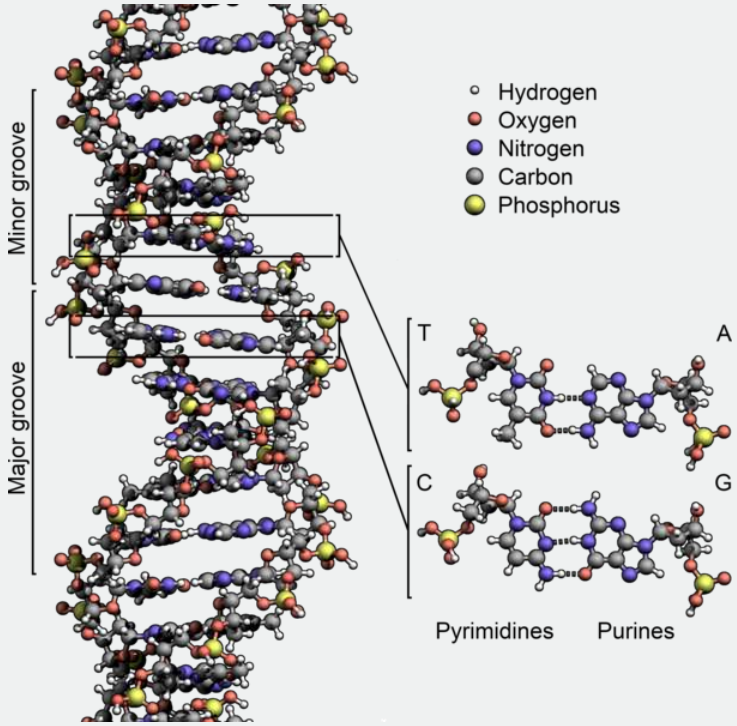


Figure 11.6.2: The DNA in our cells is a polymer of nucleotides, each of which is composed of a phosphate group, a sugar, and a nitrogen-containing base. (CC BY-SA 3.0 Unported; Zephyris via Wikipedia)

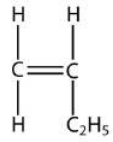
Key Takeaways

- Polymers are long molecules composed of chains of units called monomers.
- Several important biological polymers include proteins, starch, cellulose, and DNA.

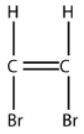
Exercise 11.6.2

1. Explain the relationship between a monomer and a polymer.
2. Must a monomer have a double bond to make a polymer? Give an example to illustrate your answer.

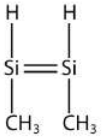
3. Draw the polymer made from this monomer.



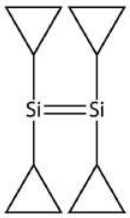
4. Draw the polymer made from this monomer.



5. What is the difference between an addition polymer and a condensation polymer?
6. What is the difference between a condensation polymer and a copolymer?
7. List three properties of polymers that vary widely with composition.
8. List three uses of polymers.
9. Draw the silicone made from this monomer.



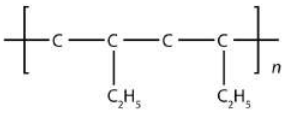
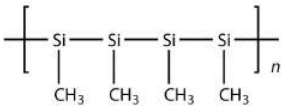
10. Draw the silicone made from this monomer.



11. Explain how starch is a polymer.
12. What is the difference between starch and cellulose?
13. Explain how protein is a polymer.
14. What are the parts that compose DNA?

Nov 27, 2021, 10:23 AM

Answers

1. A polymer is many monomers bonded together.
2. 
3.
4.
5. In an addition polymer, no small molecule is given off as a product; whereas in a condensation polymer, small parts of each monomer come off as a small molecule.
6.
7. solubility in H_2O and other solvents, melting point, flammability, color, hardness, transparency, film thickness, wetability, surface friction, moldability, and particle size (answers will vary)
8. 
9.
10.

11. Starch is composed of many glucose monomer units.
12.
13. Proteins are polymers of amino acids, which act as the monomers.

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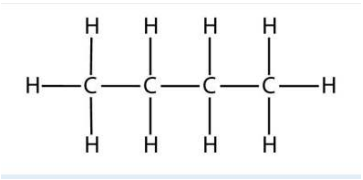
11.E: Organic Chemistry (Exercises)

Exercises (Hydrocarbons)

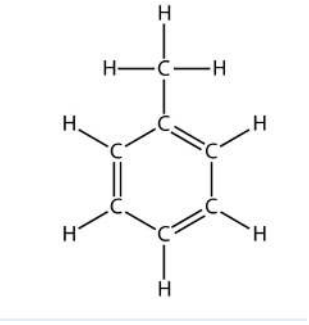
1. Define hydrocarbon. What are the two general types of hydrocarbons?

2. What are the three different types of aliphatic hydrocarbons? How are they defined?

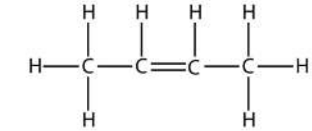
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

<smiles>CCCC</smiles>

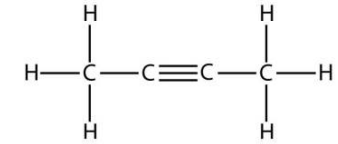
b. 

<smiles>Cc1ccccc1</smiles>

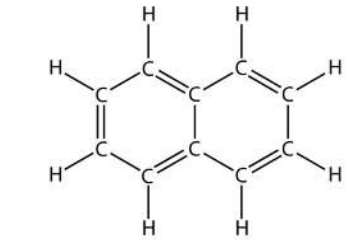
c. 

<smiles>C/C=C\C</smiles>

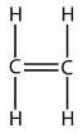
4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

<smiles>CC#CC</smiles>

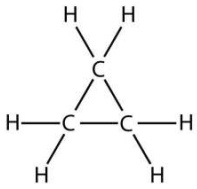
b. 

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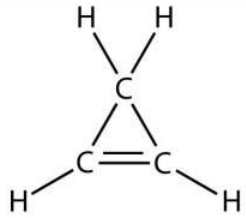
c. 

<smiles>C=C</smiles>

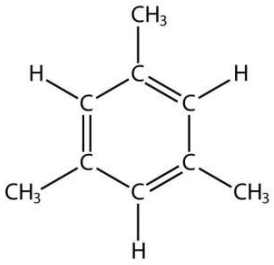
5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

<smiles>C1CC1</smiles>

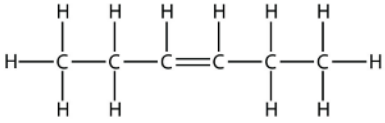
b. 

<smiles>C1=CC1</smiles>

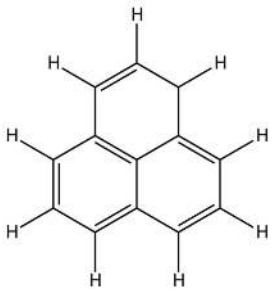
c. 

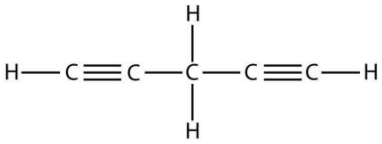
<smiles>Cc1cccc(C)c1</smiles>

6. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

<smiles>C/C=C\C</smiles>

b. 

c. 

<smiles>C#CCC#C</smiles>

7. Name and draw the structural formulas for the four smallest alkanes.

8. Name and draw the structural formulas for the four smallest alkenes.

9. What does the term aromatic imply about an organic molecule?

10. What does the term normal imply when used for alkanes?

11. Explain why the name 1-propene is incorrect. What is the proper name for this molecule?

12. Explain why the name 3-butene is incorrect. What is the proper name for this molecule?

13. Name and draw the structural formula of each isomer of pentene.

14. Name and draw the structural formula of each isomer of hexyne.

15. Write a chemical equation for the reaction between methane and bromine.

16. Write a chemical equation for the reaction between ethane and chlorine.

17. Draw the structure of the product of the reaction of bromine with propene.

18. Draw the structure of the product of the reaction of chlorine with 2-butene.

19. Draw the structure of the product of the reaction of hydrogen with 1-butene.

20. Draw the structure of the product of the reaction of hydrogen with 2-pentene.

21. Write the balanced chemical equation for the combustion of heptane.

22. Write the balanced chemical equation for the combustion of nonane.

Answers

1. an organic compound composed of only carbon and hydrogen; aliphatic hydrocarbons and aromatic hydrocarbons

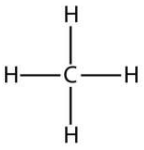
3.

a. aliphatic; alkane
b. aromatic
c. aliphatic; alkene

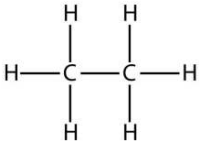
5.

a. aliphatic; alkane
b. aliphatic; alkene
c. aromatic

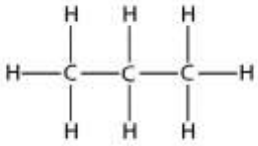
7.

a.  Methane

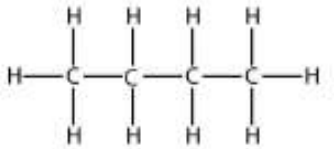
<smiles>C</smiles>

b.  Ethane

<smiles>CC</smiles>

c.  Propane

<smiles>CCC</smiles>

d.  Butane

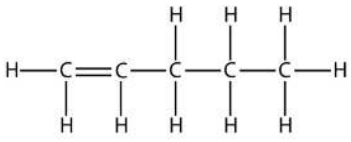
<smiles>CCCC</smiles>

9. Aromatic means that the molecule has a benzene ring.

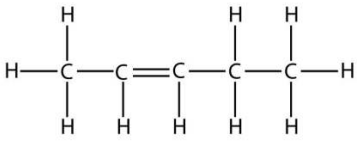
11. The 1 is not necessary. The name of the compound is simply propene.

<smiles>C=CCCC</smiles>

13.

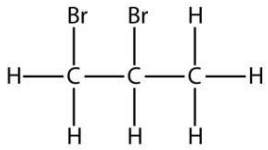
a.  1-Pentene

<smiles>C=CCCC</smiles>

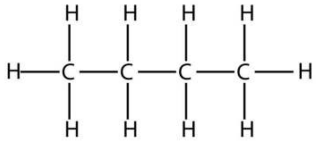
b.  2-Pentene

<smiles>CC=CCC</smiles>

15. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$

17. 

<smiles>CC(Br)CBr</smiles>

19. 

<smiles>CCCC</smiles>

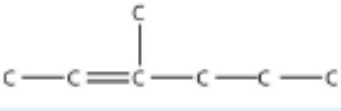
21. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

Exercises (Branched Hydrocarbons)

1. How does a branched hydrocarbon differ from a normal hydrocarbon?

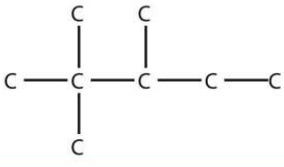
2. How does a substituent get its unique name?

3. Name this molecule.



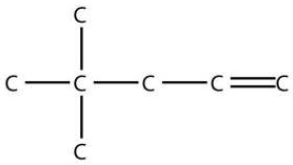
<smiles>CC=C(C)CCC</smiles>

4. Name this molecule.



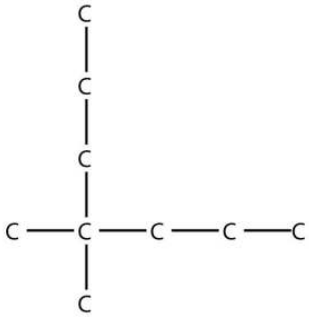
<smiles>CC(C)C(C)(C)C</smiles>

5. Name this molecule.



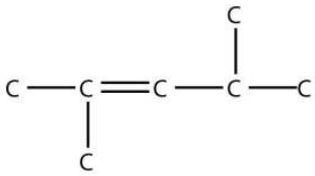
<smiles>C=CCC(C)(C)C</smiles>

6. Name this molecule.



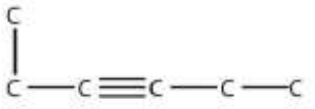
<smiles>CCCC(C)(C)CCCl</smiles>

7. Name this molecule.



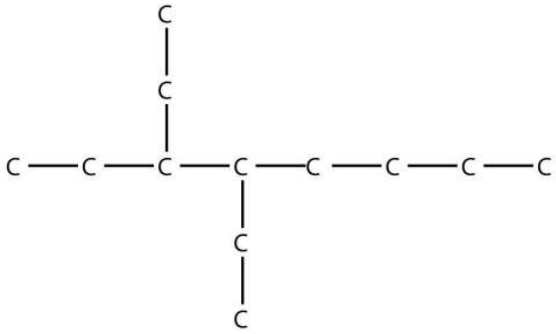
<smiles>CC(C)=CC(C)C</smiles>

8. Name this molecule.



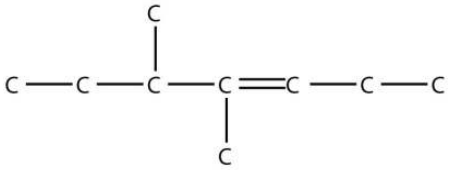
<smiles>CCC#CCC</smiles>

9. Name this molecule.



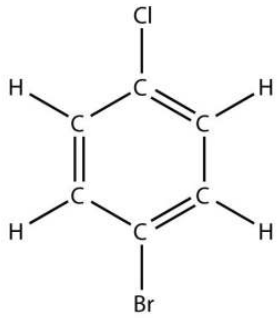
<smiles>CCCCC(CC)C(CC)CC</smiles>

10. Name this molecule.



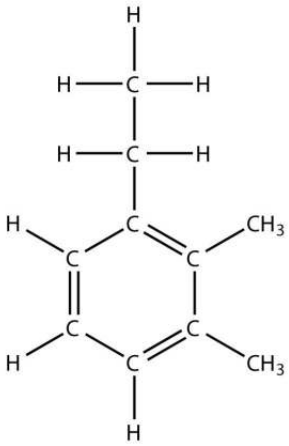
<smiles>CCC=C(C)C(C)CC</smiles>

11. Name this molecule.



<smiles>Clc1ccccc1</smiles>

12. Name this molecule.



<smiles>CCCc1ccccc1C</smiles>

13. Draw the carbon backbone for each molecule.

    a. 3,4-diethyloctane
    b. 2,2-dimethyl-4-propylnonane

14. Draw the carbon backbone for each molecule.

    a. 3-ethyl-4-methyl-3-heptene
    b. 3,3-diethyl-1-pentyne

15. Draw the carbon backbone for each molecule.

    a. 4-ethyl-4-propyl-2-octyne
    b. 5-butyl-2,2-dimethyldecane

16. Draw the carbon backbone for each molecule.

    a. 3,4-diethyl-1-hexyne
    b. 4-propyl-3-ethyl-2-methyloctane

17. The name 2-ethylhexane is incorrect. Draw the carbon backbone and write the correct name for this molecule.

18. The name 3-butyl-7-methyloctane is incorrect. Draw the carbon backbone and write the correct name for this molecule.

Answers

1. A branched hydrocarbon does not have all of its C atoms in a single row.

3. 3-methyl-2-hexene

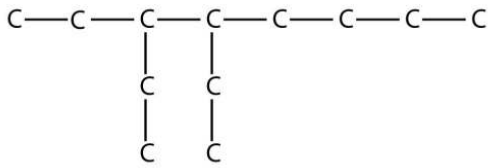
5. 4,4-dimethyl-1-pentene

7. 2,4-dimethyl-2-pentene

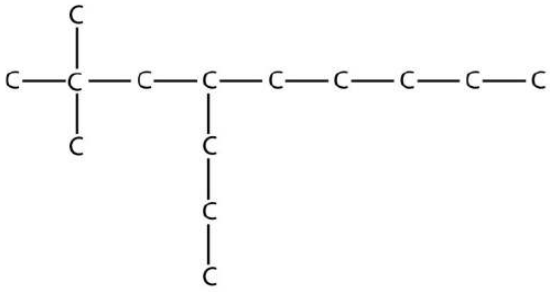
9. 3,4-diethyloctane

11. 1-bromo-4-chlorobenzene

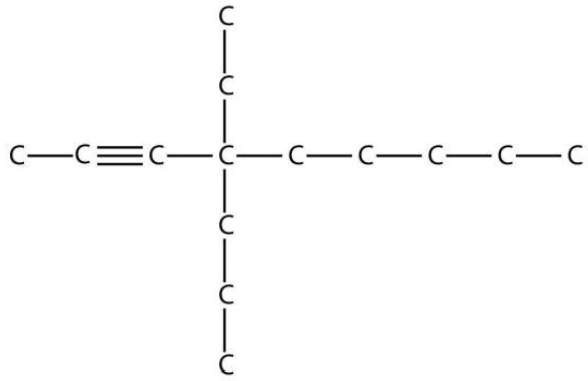
13.

a. 

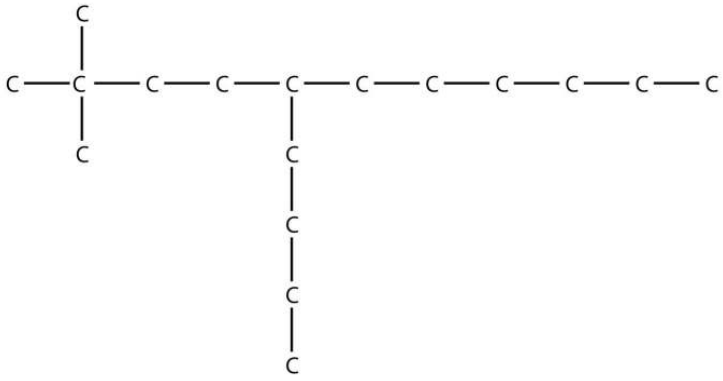
<smiles>CCCCC(CC)C(CC)CC</smiles>

b. 

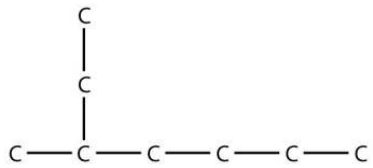
<smiles>CCCCCC(CCC)CC(C)(C)C</smiles>

15. a. 

<smiles>CC#CC(CC)(CCC)CCCCC</smiles>

b. 

<smiles>CCCCCCC(CCCC)CCC(C)(C)C</smiles>

17.  2-methylheptane

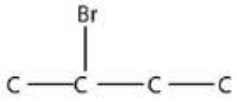
<smiles>CCCCC(C)CC</smiles>

Exercises (Alkyl Halides and Alcohols)

1. Define functional group and give two examples.

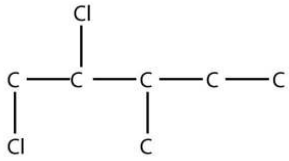
2. What is elimination? How does it differ for alkyl halides and alcohols?

3. Name this molecule.



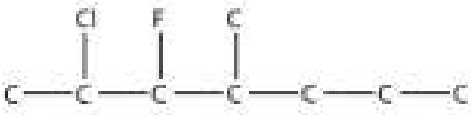
<smiles>CC(C)Br</smiles>

4. Name this molecule.



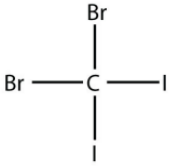
<smiles>CCC(C)C(Cl)CCl</smiles>

5. Name this molecule.



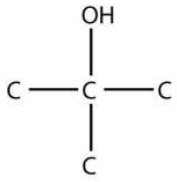
<smiles>CCCC(C)C(F)C(C)Cl</smiles>

6. Name this molecule.



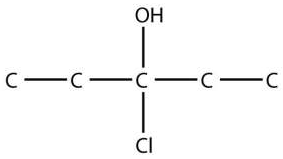
<smiles>BrC(Br)(I)I</smiles>

7. Name this molecule.



<smiles>CC(C)(C)O</smiles>

8. Name this molecule.



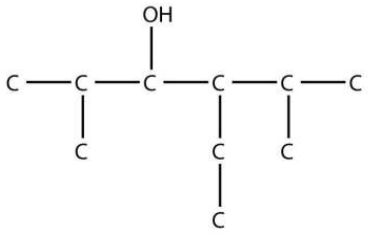
<smiles>CCC(O)(Cl)CC</smiles>

9. Name this molecule.



<smiles>CCCCC(O)CCCl</smiles>

10. Name this molecule.



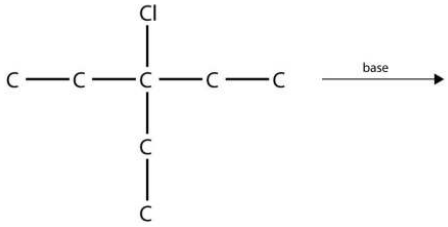
<smiles>CCC(C(C)C)C(O)C(C)C</smiles>

11. Predict the product(s) of this elimination reaction.



<smiles>CCC(O)CC</smiles>

12. Predict the product(s) of this elimination reaction.



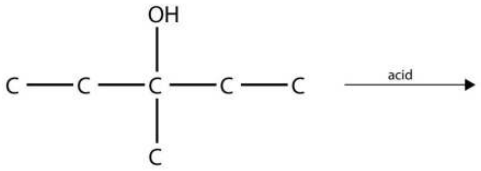
<smiles>CCC(Cl)(CC)CC</smiles>

13. Predict the product(s) of this elimination reaction.



<smiles>CCCC(Br)CC</smiles>

14. Predict the product(s) of this elimination reaction.



<smiles>CCC(C)(O)CC</smiles>

Answers

1. a group of atoms with a certain reactivity; halogen atoms and alcohol groups (answers will vary).

3. 2-bromobutane

5. 2-chloro-3-fluoro-4-methylheptane

7. 2-methyl-2-propanol

9. 4-octanol

11. 2-pentene

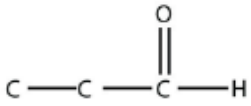
13. 2-hexene and 3-hexene

Exercises (Other Oxygen-Containing Functional Groups)

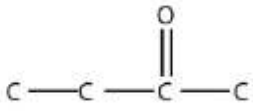
1. Name a similarity between the functional groups found in aldehydes and ketones. Can you name a difference between them?

2. Explain how a carboxylic acid is used to make an ester.

3. Name each molecule.

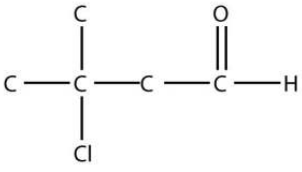
a. 

<smiles>CCC=O</smiles>

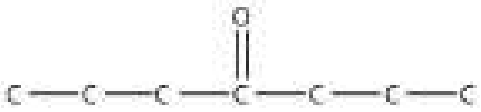
b. 

<smiles>CCC(=O)Cl</smiles>

4. Name each molecule.

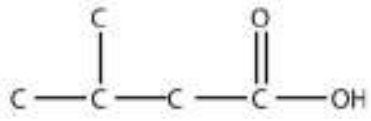
a. 

<smiles>CC(C)(Cl)CC=O</smiles>

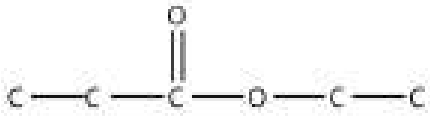
b. 

<smiles>CCCC(=O)CCC</smiles>

5. Name each molecule.

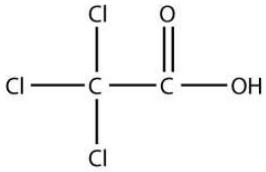
a. 

<smiles>CC(C)CC(=O)O</smiles>

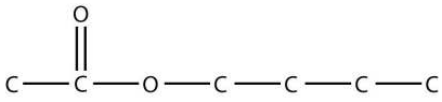
b. 

<smiles>CCC(=O)OCCl</smiles>

6. Name each molecule.

a. 

<smiles>O=C(O)C(Cl)(Cl)Cl</smiles>

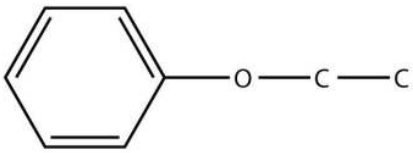
b. 

<smiles>CCCCOC(C)=O</smiles>

7. Name this molecule.



8. Name this molecule.



<smiles>CCOc1ccccc1</smiles>

9. Give an alternate but acceptable name to the molecule in Exercise 3b.

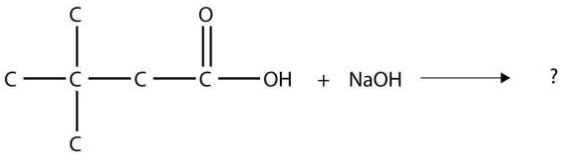
10. Give an alternate but acceptable name to the molecule in Exercise 4 b.

11. Complete this chemical reaction.



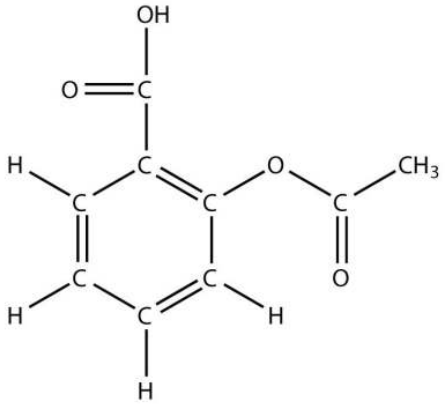
<smiles>CCC(=O)[OH2+]</smiles>

12. Complete this chemical reaction.



<smiles>CC(C)(C)CC(=O)O</smiles>

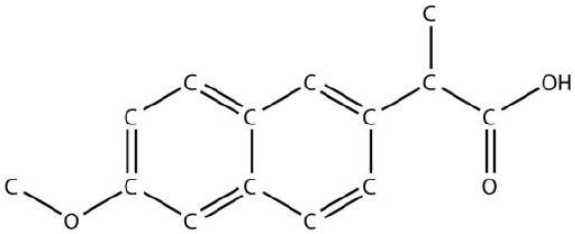
13. The drug known as aspirin has this molecular structure:



<smiles>CC(=O)Oc1ccccc1</smiles>

Identify the functional group(s) in this molecule.

14. The drug known as naproxen sodium is the sodium salt of this molecule:



<smiles>COc1ccc2cc(C(C)C(=O)O)ccc2c1</smiles>

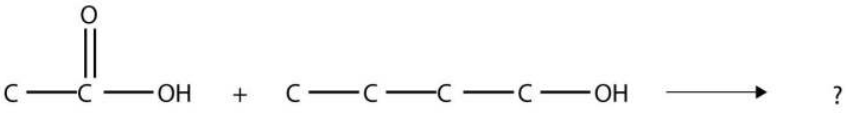
(The extra H atoms are omitted for clarity.) Identify the functional group(s) i this molecule.

15. Identify the ester made by reacting these molecules.



<smiles>CCC(=O)[OH2+]</smiles>

16. Identify the ester made by reacting these molecules.



https://chem.libretexts.org/@go/page/469503

Answers

1. They both have a carbonyl group, but an aldehyde has the carbonyl group at the end of a carbon chain, and a ketone has the carbonyl group in the middle.

3. a. propanal
   b. 2-butanone

5. a. 3-methylbutanoic acid
   b. ethyl propionate

7. ethyl propyl ether

9. ethyl methyl ketone

11. $H_2O + KCH_3CH_2CO_2$

13. acid, ester, and aromatic (benzene ring)

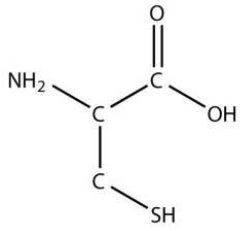
15. propyl propionate

Exercises (Other Functional Groups)

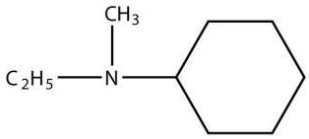
1. What are the structure and name of the smallest amine?

2. What are the structure and name of the smallest thiol?

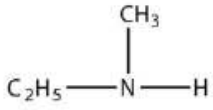
3. Identify each compound as a primary, secondary, or tertiary amine.

a. 

<smiles>NC(CS)C(=O)O</smiles>

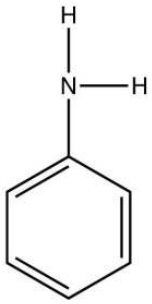
b. 

<smiles>CCN(C)C1CCCCC1</smiles>

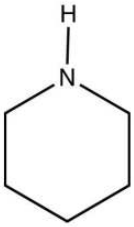
c. 

<smiles>CCNC</smiles>

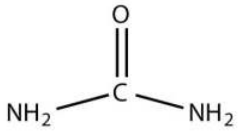
4. Identify each compound as a primary, secondary, or tertiary amine.

a. 

<smiles>Nc1ccccc1</smiles>

b. 

<smiles>C1CCNCC1</smiles>

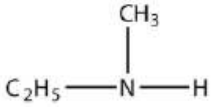
c. 

<smiles>NC(N)=O</smiles>

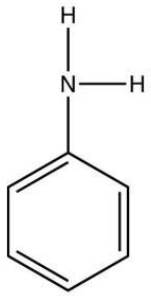
5. Write the chemical reaction between each amine in Exercise 3 and HCl.

6. Write the chemical reaction between each amine in Exercise 4 and $\mathrm{HNO_3}$.

7. Name each amine.

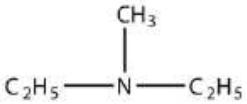
a. 

<smiles>CCNC</smiles>

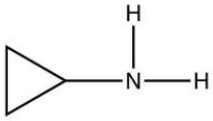
b. 

<smiles>Nc1ccccc1</smiles>

8. Name each amine.

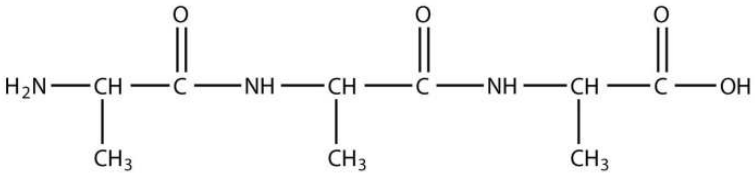
a. 

<smiles>CCN(C)CC</smiles>

b. 

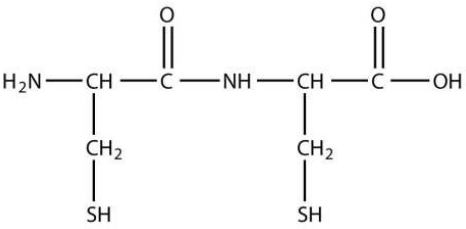
<smiles>CNC1CC1</smiles>

9. A peptide is a short chain of amino acids connected by amide bonds. How many amide bonds are present in this peptide?



<smiles>CC(N)C(=O)NC(C)C(=O)NC(C)C(=O)O</smiles>

10. How many amide bonds are present in this peptide? (See Exercise 9 for the definition of a peptide.)

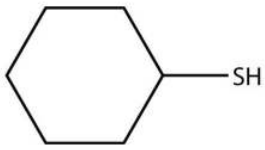


<smiles>NC(CS)C(=O)NC(CS)C(=O)O</smiles>

11. Draw the backbone structure of the amide formed by reacting propylamine with propanoic acid.

12. Draw the backbone structure of the amide formed by reacting hexylamine with ethanoic acid.

13. Name each thiol using the -thiol suffix.

a. 

b. $C_4H_9 - SH$

14. Name each thiol in Exercise 13 with the mercaptan label.

15. One component of skunk spray is 3-methyl-1-butanethiol. Draw its structure. (The 1 indicates the position of the S atom.)

16. An S-S bond can be fairly easily broken into proteins, yielding two lone cysteine units in a protein chain. Is this process an oxidation or a reduction? Explain your answer.

Answers

1. CH_3NH_2; methylamine

3.

a. primary
b. tertiary
c. secondary

5.

a. $C_3H_3CO_2HSHNH_2 + HCl \rightarrow C_3H_3CO_2HSHNH_3Cl$
b. $(C_6H_{11})(C_2H_5)(CH_3)N + HCl \rightarrow (C_6H_{11})(C_2H_5)(CH_3)NHCl$
c. $(C_2H_5)(CH_3)NH + HCl \rightarrow (C_2H_5)(CH_3)NH_2Cl$

7.

a. ethylmethylamine
b. phenylamine

9. two

11.

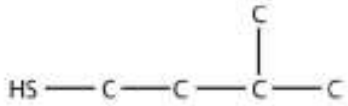


<smiles>CCCNC(=O)CC</smiles>

13.

a. cyclohexanethiol
b. butanethiol

15.



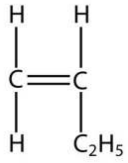
<smiles>CC(C)CCS</smiles>

Exercises (Polymers)

1. Explain the relationship between a monomer and a polymer.

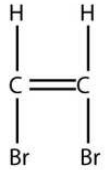
2. Must a monomer have a double bond to make a polymer? Give an example to illustrate your answer.

3. Draw the polymer made from this monomer.



<smiles>C=CCC</smiles>

4. Draw the polymer made from this monomer.



<smiles>Br/C=C/Br</smiles>

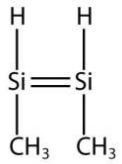
5. What is the difference between an addition polymer and a condensation polymer?

6. What is the difference between a condensation polymer and a copolymer?

7. List three properties of polymers that vary widely with composition.

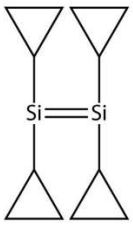
8. List three uses of polymers.

9. Draw the silicone made from this monomer.



<smiles>C[SiH]=[SiH]</smiles>

10. Draw the silicone made from this monomer.



11. Explain how starch is a polymer.

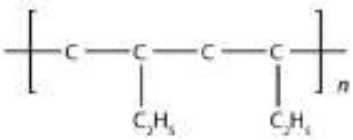
12. What is the difference between starch and cellulose?

13. Explain how protein is a polymer.

14. What are the parts that compose DNA?

Answers

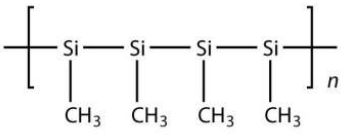
1. A polymer is many monomers bonded together.

3. 

<smiles>CCC(CCC(C)(C)CC)C(C)(C)C</smiles>

5. In an addition polymer, no small molecule is given off as a product, whereas in a condensation polymer, small parts of each monomer come off as a small molecule.

7. solubility in H_2O and other solvents, melting point, flammability, color, hardness, transparency, film thickness, wetability, surface friction, moldability, and particle size (answers will vary)

9. 

<smiles>C[SiH](C)[SiH](C)[SiH](C)[SiH](C)C</smiles>

11. Starch is composed of many glucose monomer units.

13. Proteins are polymers of amino acids, which act as the monomers.

Additional Exercises

1. Cycloalkanes are named based on the number of C atoms in them, just like regular alkanes, but with the prefix cyclo- on the name. What are the names of the three smallest cycloalkanes?

2. Cycloalkenes are named similarly to cycloalkanes (see Exercise 1). What are the names of the cycloalkenes with five, six, and seven C atoms?

3. Draw the carbon backbone of all noncyclic alkanes with only four C atoms.

4. Draw the carbon backbone of all noncyclic alkanes with only five C atoms.

5. Cyclic alkanes can also have substituent groups on the ring. Draw the carbon backbone of all cyclic alkanes with only four C atoms.

6. Cyclic alkanes can also have substituent groups on the ring. Draw the carbon backbone of all cyclic alkanes with only five C atoms.

7. Draw and name all possible isomers of pentene.

8. Draw and name all possible normal (that is, straight-chain) isomers of heptyne.

9. Polyunsaturated alkenes have more than one $\mathrm{C}-\mathrm{C}$ double bond. Draw the carbon backbone of all possible noncyclic polyunsaturated alkenes with four C atoms and two double bonds. What are the complete molecular formulas for each possible molecule?

10. Draw the carbon backbone of all possible five-carbon cyclic alkenes with two double bonds, assuming no substituents on the ring.

11. If a hydrocarbon is combined with enough halogen, all the H atoms will eventually be substituted with that halogen atom. Write the balanced chemical reaction between ethane and excess chlorine.

12. If a hydrocarbon is combined with enough halogen, all the H atoms will eventually be substituted with that halogen atom. Write the balanced chemical reaction between butane and excess bromine.

13. Molecules with multiple double bonds can also participate in addition reactions. Draw the structure of the product when butadiene, $\mathrm{CH_2=CH-CH=CH_2}$, reacts with chlorine.

14. Molecules with multiple double bonds can also participate in addition reactions. Draw the structure of the product when allene, $\mathrm{CH_2=C=CH_2}$, reacts with bromine.

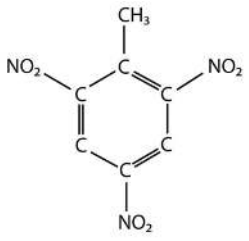
15. What is the maximum number of methyl groups that can be on a propane backbone before the molecule cannot be named as a propane compound?

16. Explain why cycloethane cannot exist as a real molecule.

17. In the gasoline industry, what is called isooctane is actually 2,2,4-trimethylpentane. Draw the structure of isooctane.

18. Isooctane (see Exercise 17) is an isomer of what straight-chain alkane?

19. The actual name for the explosive TNT is 2,4,6-trinitrotoluene. If the structure of TNT is



<smiles>Cc1c([N+](=O)[O-])cc([N+](=O)[O-])cc1[N+](=O)[O-]</smiles>

propose the structure of the parent compound toluene.

20. Phenol is hydroxybenzene, the simplest aromatic alcohol. Picric acid is an explosive derivative of phenol whose formal name is 2,4,6-trinitrophenol. With reference to Exercise 19, draw the structure of picric acid.

21. Draw the structures of all possible straight-chain isomers of bromopentane.

22. Draw the structures of all the possible isomers of butanol. Include branched isomers.

23. What is the final product of the double elimination of HCl from 1,1-dichloroethane?

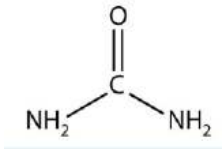
24. Draw the structure of the final product of the double elimination of 1,3-dibromopropane.

25. Draw the structure and name of the alcohol whose double elimination would yield the same product as in Exercise 23. Name the molecule as a hydroxylsubstituted compound.

26. Draw the structure and name of the alcohol whose double elimination would yield the same product as in Exercise 24. Name the molecule as a hydroxylsubstituted compound.

27. Draw the smallest molecule that can have a separate aldehyde and carboxylic acid group.

28. Name the functional group(s) in urea, a molecule with the following structure:



<smiles>NC(N)=O</smiles>

29. Ethyl acetate is a common ingredient in nail-polish remover because it is a good solvent. Draw the structure of ethyl acetate.

30. A lactone is an ester that has its ester functional group in a ring. Draw the structure of the smallest possible lactone (which is called acetolactone, which might give you a hint about its structure).

31. Draw the structure of diethyl ether, once used as an anesthetic.

32. The smallest cyclic ether is called an epoxide. Draw its structure.

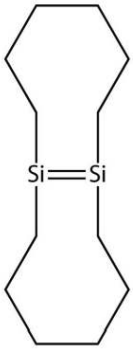
33. The odor of fish is caused by the release of small amine molecules, which vaporize easily and are detected by the nose. Lemon juice contains acids that react with the amines and make them not as easily vaporized, which is one reason why adding lemon juice to seafood is so popular. Write the chemical reaction of HCl with trimethylamine, an amine that is given off by seafood.

34. Putrescine and cadaverine are molecules with two amine groups on the opposite ends of a butane backbone and a pentane backbone, respectively. They are both emitted by rotting corpses. Draw their structures and determine their molecular formulas.

35. With four monomers, draw two possible structures of a copolymer composed of ethylene and propylene.

36. With four monomers, draw two possible structures of a copolymer composed of ethylene and styrene.

37. Draw the silicone that can be made from this monomer:

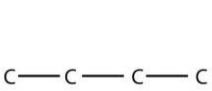


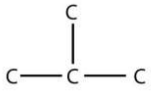
38. One of the ingredients in the original Silly Putty was a silicone polymer with two methyl groups on each Si atom. Draw this silicone.

Answers

1. cyclopropane, cyclobutane, and cyclopentane

3.

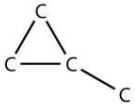




<smiles>CC(C)C</smiles>

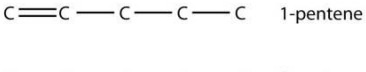
5.



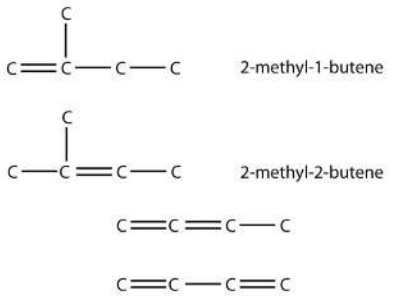


<smiles>C1CCC1</smiles> <smiles>CC1CC1</smiles>

7.



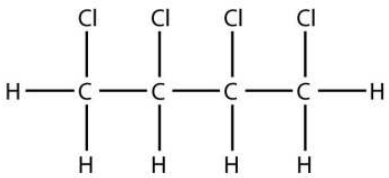
9.



Both molecular formulas are C_4H_6.

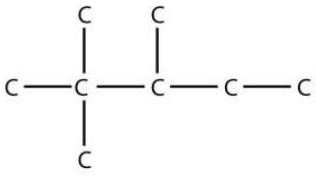
11. $C_2H_6 + 6Cl_2 \rightarrow C_2Cl_6 + 6HCl$

13.

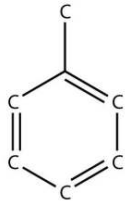


<smiles>CCl</smiles>

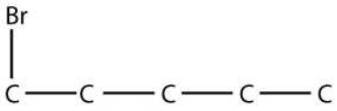
15. two

17. 

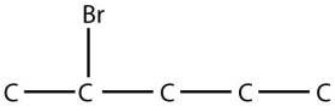
<smiles>CCC(C)C(C)(C)C</smiles>

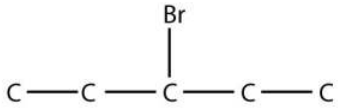
19. 

<smiles>CCCCCBr</smiles>



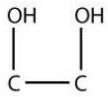
<smiles>CCCC(C)Br</smiles>



21. 

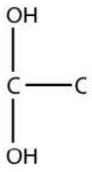
<smiles>CCC(Br)CC</smiles>

23. ethyne



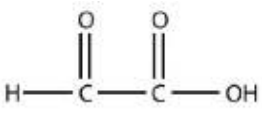
<smiles>OCCO</smiles>

or



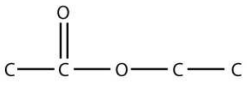
<smiles>OC(O)Cl</smiles>

25. The names are 1,2-dihydroxyethane and 1,1-dihydroxyethane, respectively.

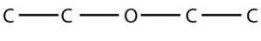
27. 

https://chem.libretexts.org/@go/page/469503

<smiles>O=CC(=O)O</smiles>

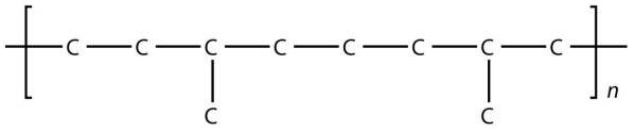
29. 

<smiles>CCOC(C)=O</smiles>

31. 

33. $(CH_3)_3\ N + HCl \rightarrow (CH_3)_3\,NHCl$

35. (answers will vary)

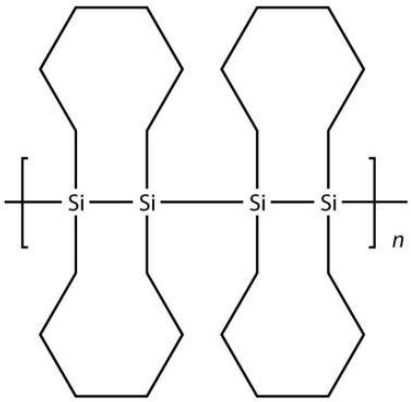


<smiles>CC(CCCCC(C)(C)C)CCC(C)(C)C</smiles>

or



<smiles>CC(CCCCC(C)CC(C)(C)C)CC(C)(C)C</smiles>

37. 

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  - 12.1.1: Important Hexoses
  - 12.1.2: Properties of Monosaccharides
  - 12.1.3: Disaccharides
  - 12.1.4: Polysaccharides
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  - 12.2.1: Fats and Oils
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12.0: An Introduction to Biochemistry

Learning Objectives

- Explain what a biomolecule is and list the four main types.

Biochemistry is the study of the molecules of life, (**biomolecules**); those that structurally make up living organisms and function to keep them alive. Although the complexity of biomolecules ranges from individual small molecules, such as glycine, to very large complexes made up of multiple molecules linked together, like ATP synthase, most biomolecules can be categorized into for main groups based on their structural similarities: *carbohydrates*, *proteins*, *lipids*, or *nucleic acids*. There are also many other small molecules and ions that play a wide variety of roles in the cell, ranging chemical messengers (or signals), to toxins produced as a means of defense against invaders, to coordination complexes that play important rolls in protein function.

Now that you have learned the basics of general and organic chemistry, you are ready to apply your knowledge to understanding the chemistry of these biomolecules. You will recognize some of the organic functional groups in these biomolecules, which will help you predict the physical and chemical properties of these new molecules. Living cells are very complex, however, the same principles that govern chemistry apply to all of biochemistry.

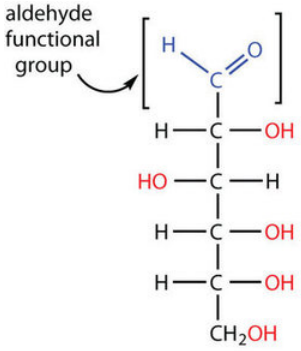
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12.1: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

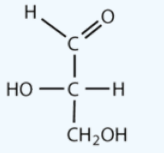
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. 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 $C_6{\cdot}6H_2O$.

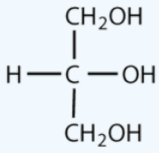


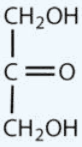
Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

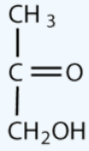
Example 12.1.1

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.

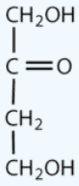
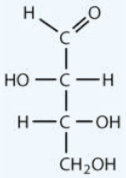
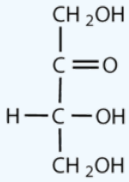
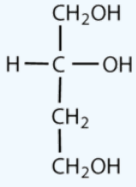
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.

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 12.1.1

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:

$$6\,CO_2 + 6\,H_2O + 686\text{ kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{12.1.1}$$

(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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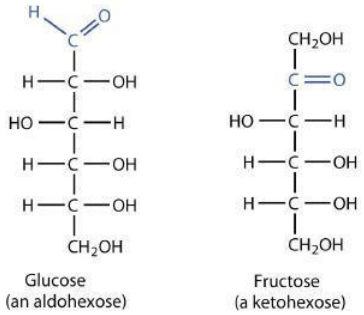
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12.1.0: Classes of Monosaccharides

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.



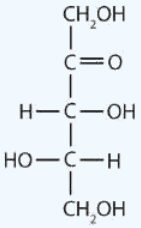
Example 12.1.0.1

Draw an example of each type of compound.

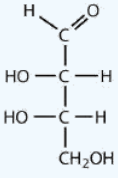
a. a ketopentose
b. an aldotetrose

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 12.1.0.1

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 12.1.0.1; 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 12.1.0.1. 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.

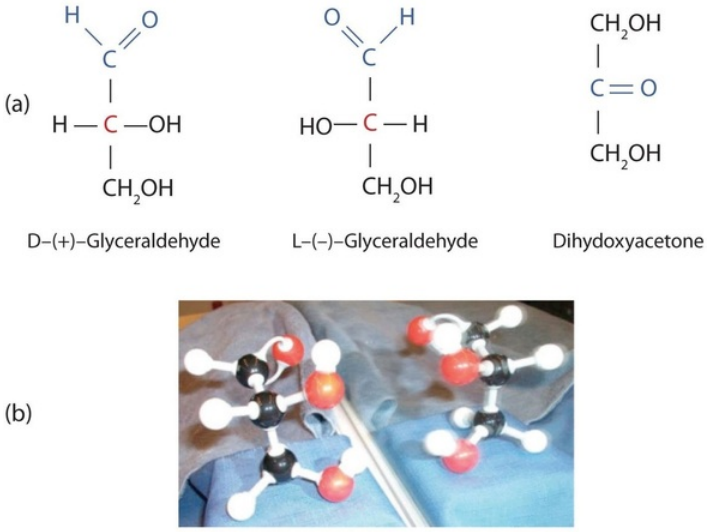


Figure 12.1.0.1: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

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 12.1.0.1). 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°.

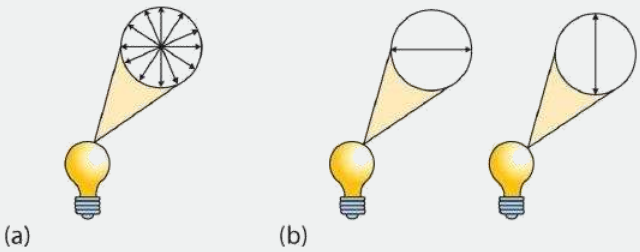
H. Emil Fischer, a German chemist, developed the convention commonly used for writing two-dimensional representations of the monosaccharides, such as those in part (a) of Figure 12.1.0.1. In these structural formulas, the aldehyde group is written at the top, and the hydrogen atoms and OH groups that 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.

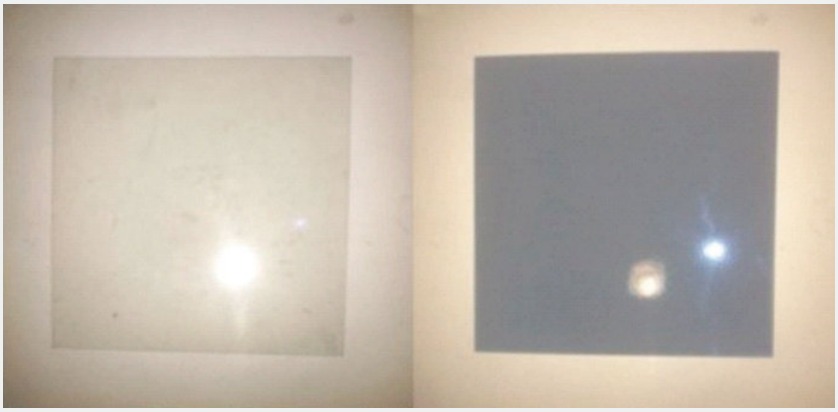
> *By convention, the penultimate (next-to-last) carbon atom has been chosen as the carbon atom that determines if a sugar is D or L. It is the chiral carbon farthest from the aldehyde or ketone functional group.*

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.

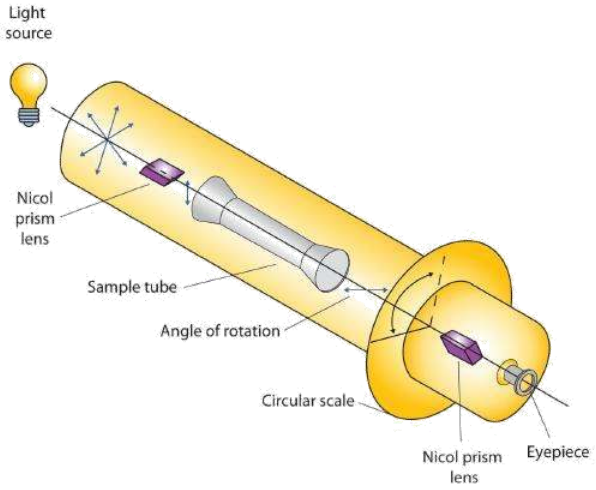


Figure 12.1.0.2: Diagram of a Polarimeter

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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12.1.1: 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 12.1.1.1). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

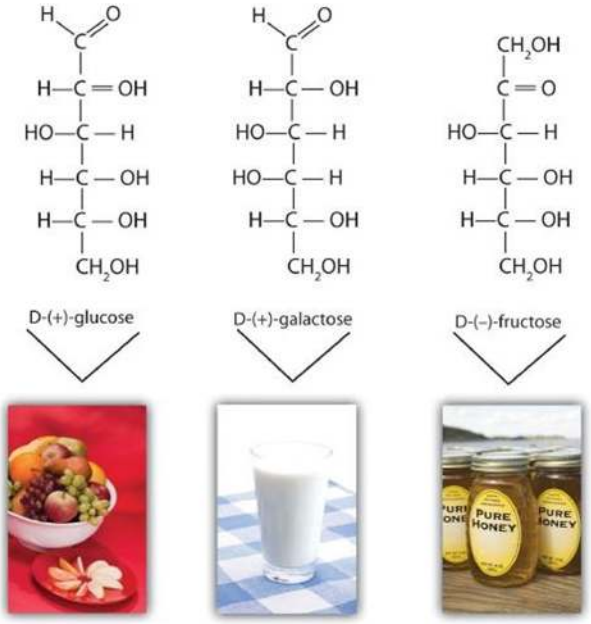


Figure 12.1.1.1: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

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.

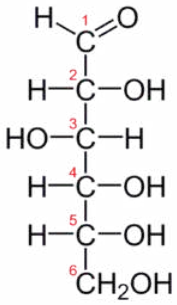


Figure 12.1.1.2: Fischer projection of D-glucose

The Fischer projection of D-glucose is given in Figure 12.1.1.2. 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 12.1.1.1. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure 12.1.1.1, 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 12.1.1.1).

Table 12.1.1.1: 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

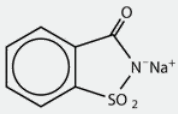
Looking Closer: Artificial Sweeteners

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.

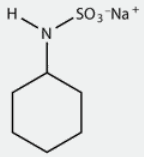
The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short 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

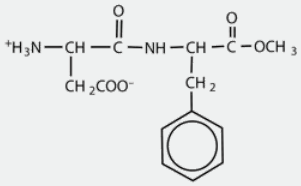
bladder cancer in rats. The US Food and Drug Administration (FDA) proposed a ban on saccharin that raised immediate public opposition because saccharin was the only artificial sweetener still available. In response, Congress passed the Saccharin Study and Labeling Act in 1977, permitting the use of saccharin 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.



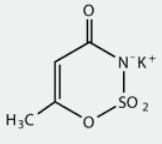
Saccharin



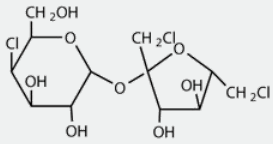
Cyclamate



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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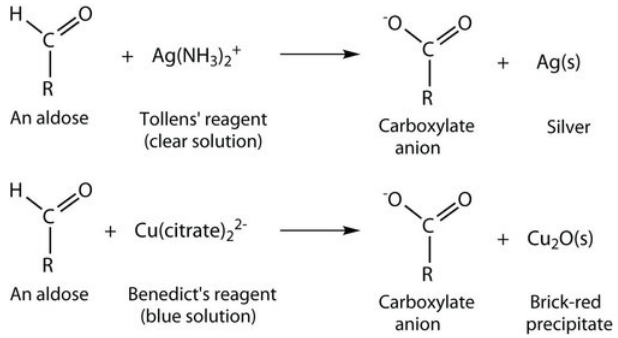
12.1.2: Properties of Monosaccharides

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 12.1.2.1].



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*.

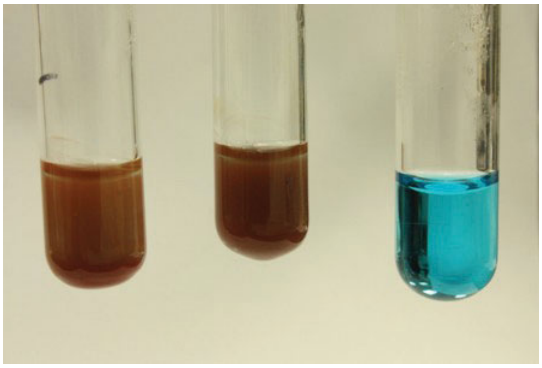


Figure 12.1.2.1: Benedict's Test. Benedict's test was performed on three carbohydrates, depicted from left to right: fructose, glucose, and sucrose. The solution containing sucrose remains blue because sucrose is a nonreducing sugar.

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.

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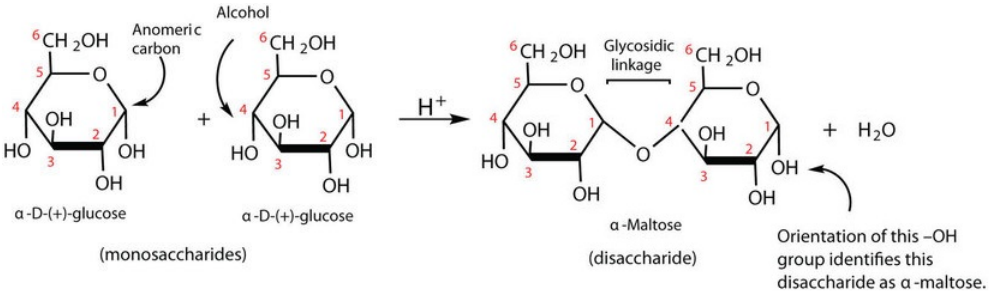
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12.1.3: Disaccharides

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 12.1.3.1). 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 12.1.3.1.

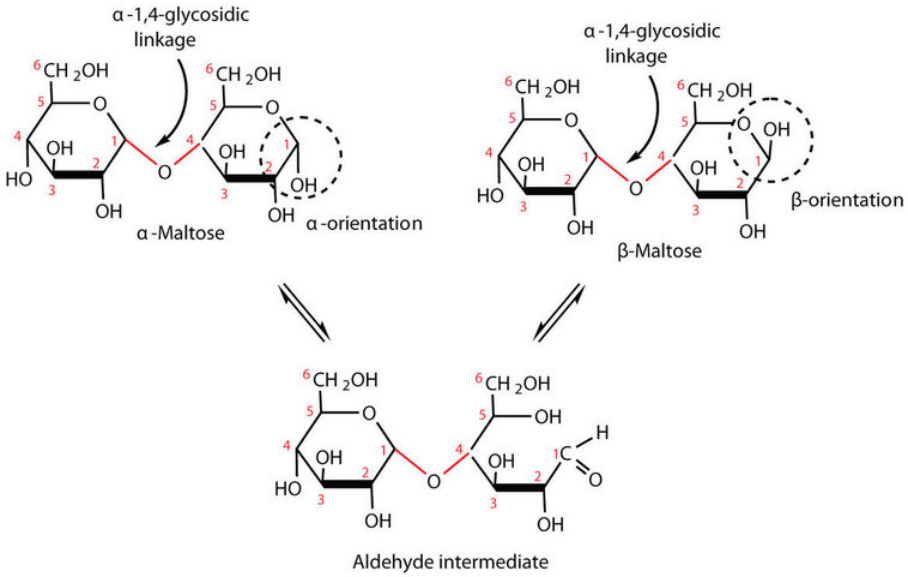
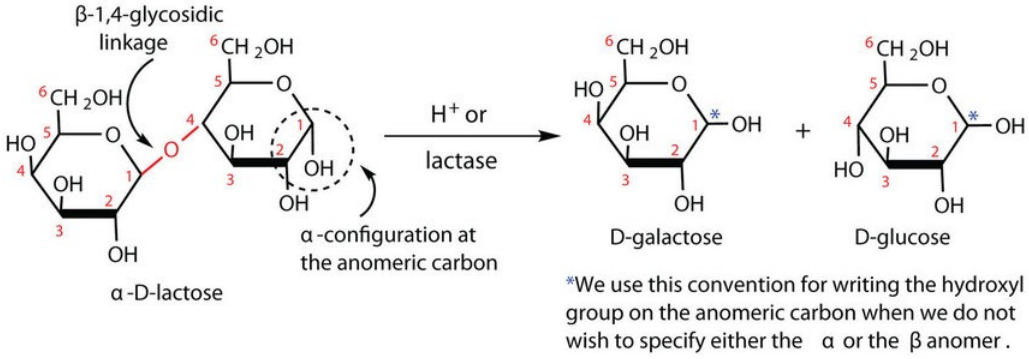


Figure 12.1.3.1: An Equilibrium Mixture of Maltose Isomers

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.

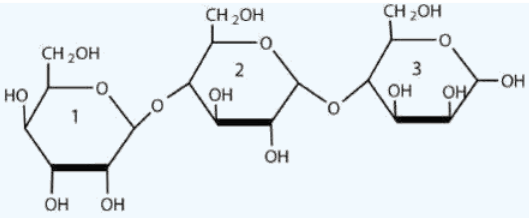
Lactose is a reducing sugar composed of one molecule of D-galactose and one molecule of D-glucose joined by a β-1,4-glycosidic bond (the bond from the anomeric carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic 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 12.1.3.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.

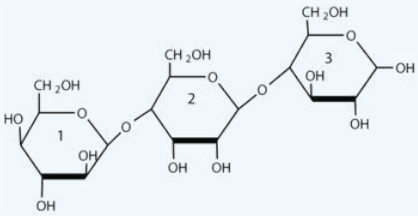


Solution

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 12.1.3.1

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.

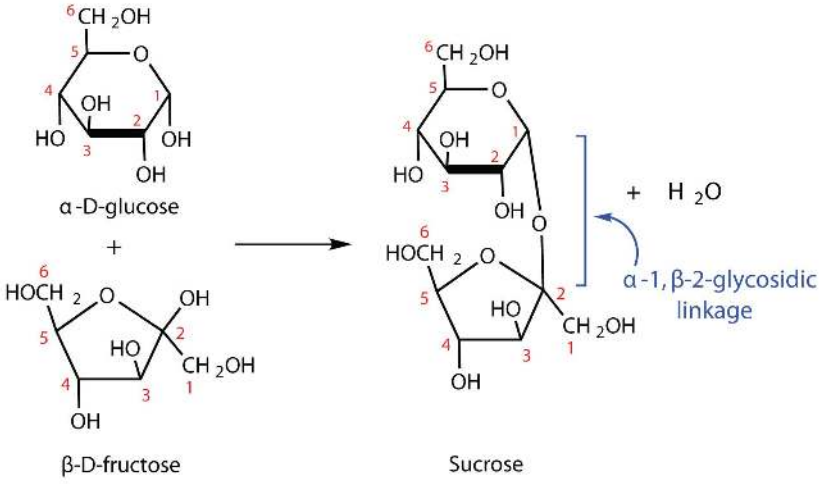
The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis 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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12.1.4: 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 12.1.4.1). 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 12.1.4.1). 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.

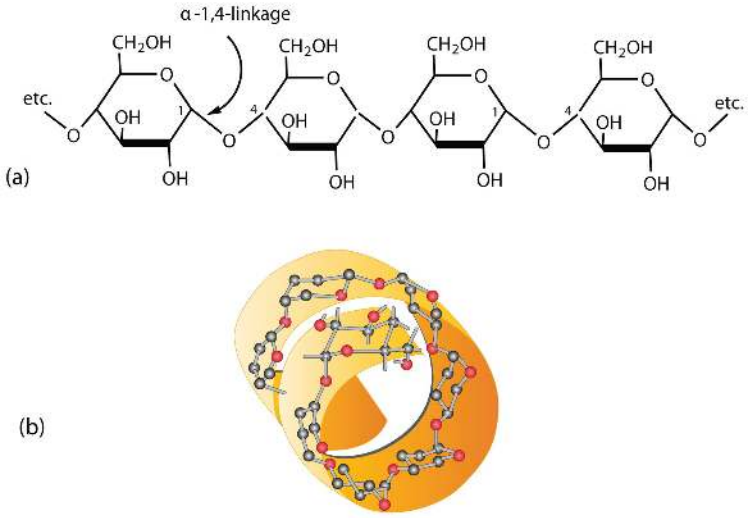


Figure 12.1.4.1: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

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 12.1.4.2). 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.

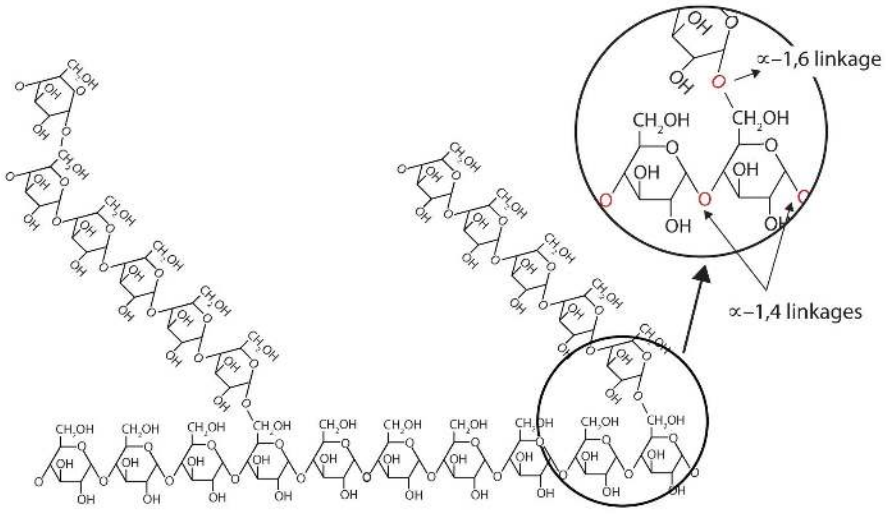


Figure 12.1.4.2: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

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 12.1.4.3). 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 12.1.4.3). 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.

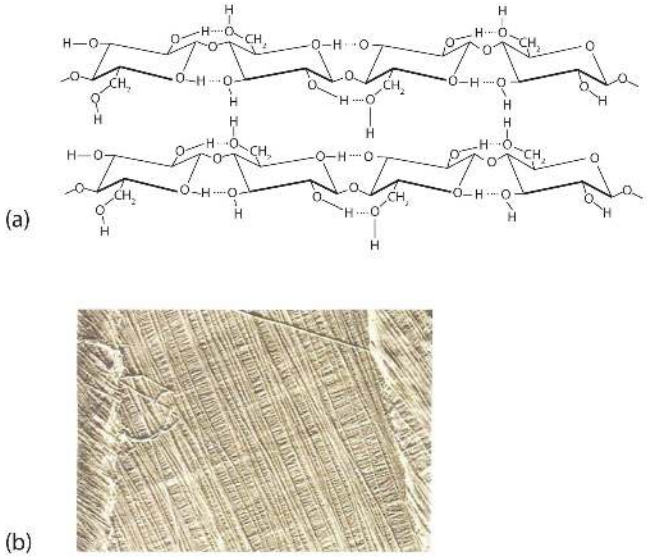


Figure 12.1.4.3: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

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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12.2: 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 12.2.1 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.

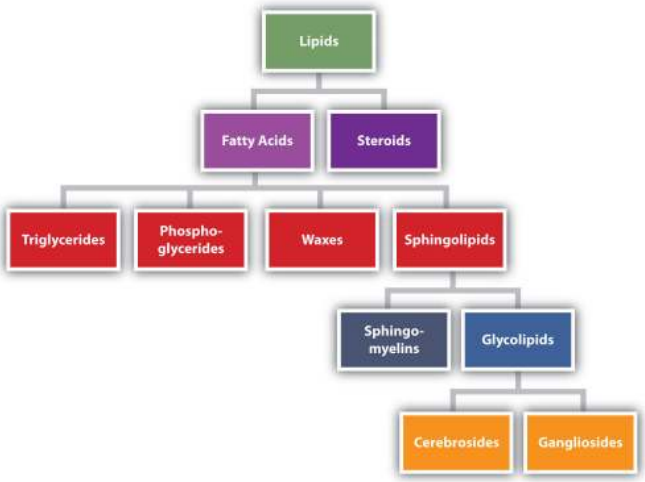


Figure 12.2.1: Lipid Organization Based on Structural Relationships

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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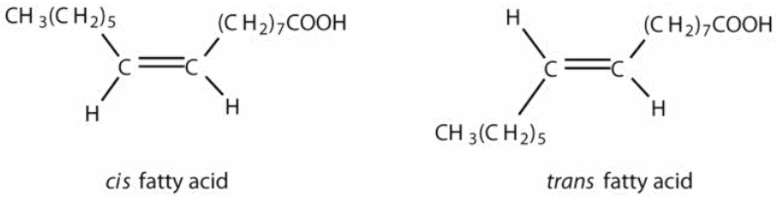
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12.2.0: Fatty Acids

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 12.2.0.1 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 12.2.0.1: Some Common Fatty Acids Found in Natural Fats

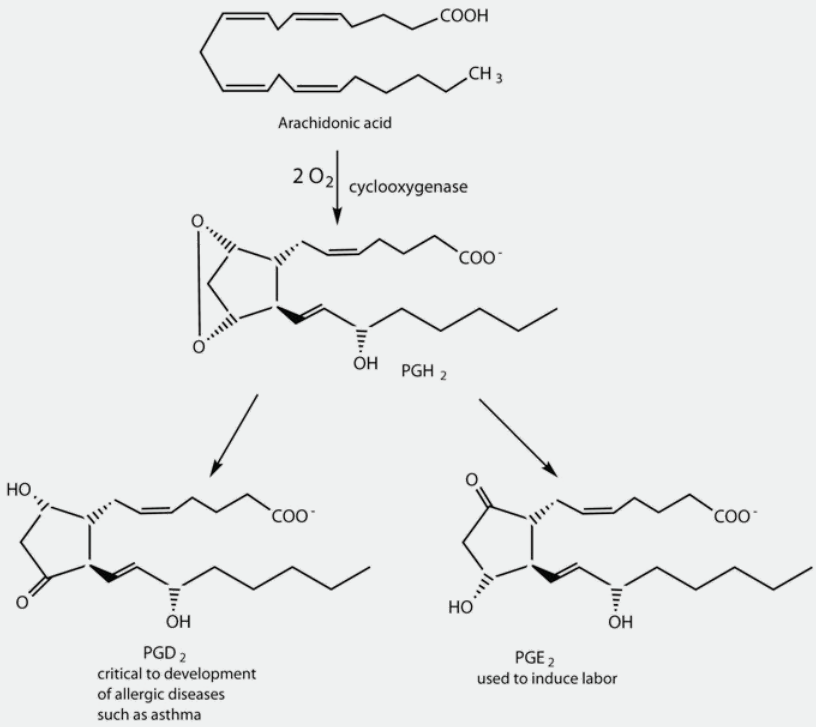
Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
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 12.2.0.2*a*). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure 12.2.0.2*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.

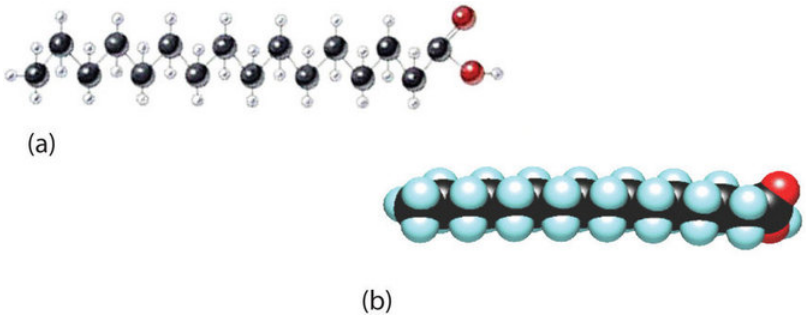
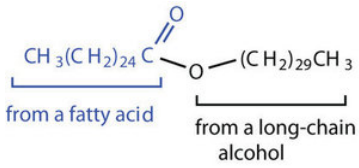


Figure 12.2.0.2: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

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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12.2.1: Fats and Oils

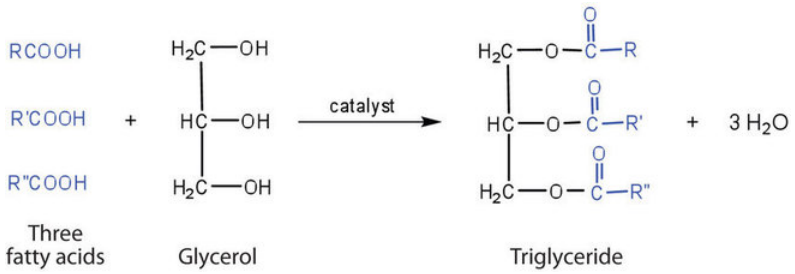
Learning Objectives

- 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.

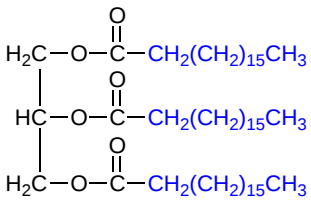
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

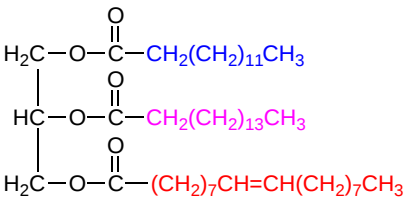
Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



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*.



Tristearin
a simple triglyceride



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 12.2.1.1 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 12.2.1.1: 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

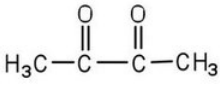
*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

†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.

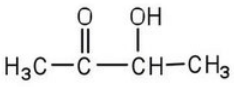
Terms such as *saturated fat* or *unsaturated oil* are often used to describe the fats or oils obtained from foods. Saturated fats contain a high proportion of saturated fatty acids, while unsaturated oils contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is 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

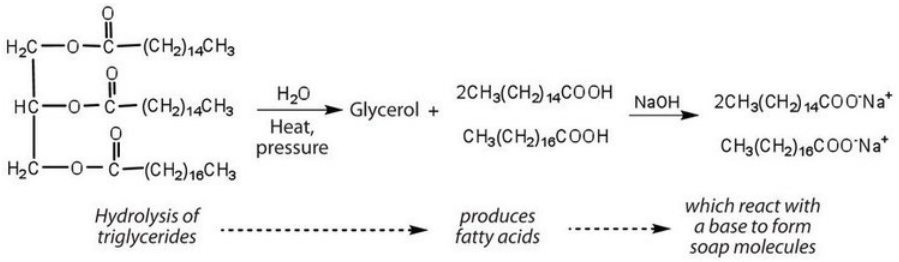


3-hydroxy-2-butanone

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

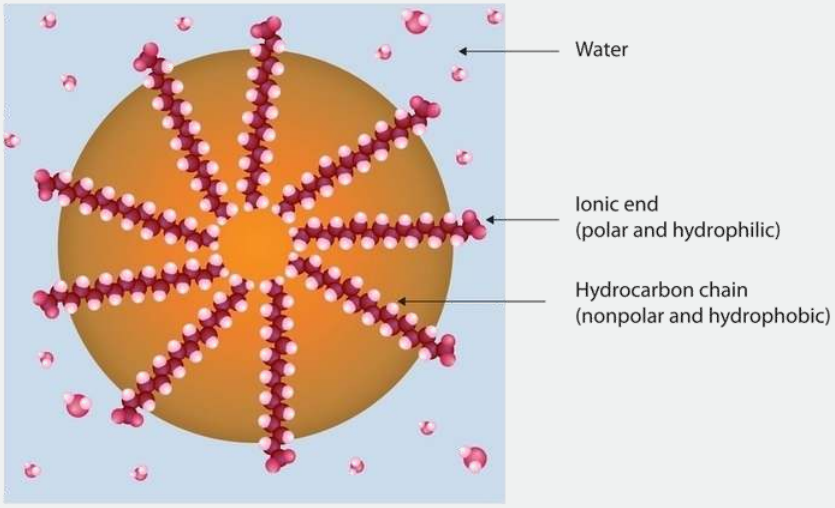
Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called 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

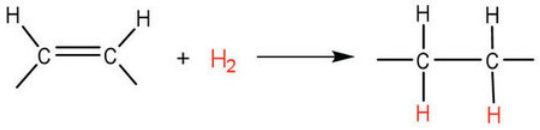
Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, 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.

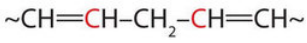


In commercial processes, the number of double bonds that are hydrogenated is carefully controlled to produce fats with the desired consistency (soft and pliable). Inexpensive and abundant vegetable oils (canola, corn, soybean) are thus transformed into margarine and cooking fats. In the preparation of 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.

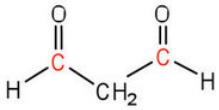
Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* 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.

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12.2.2: 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 12.2.2.1A) and animal cells (Figure 12.2.2.1B) 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.

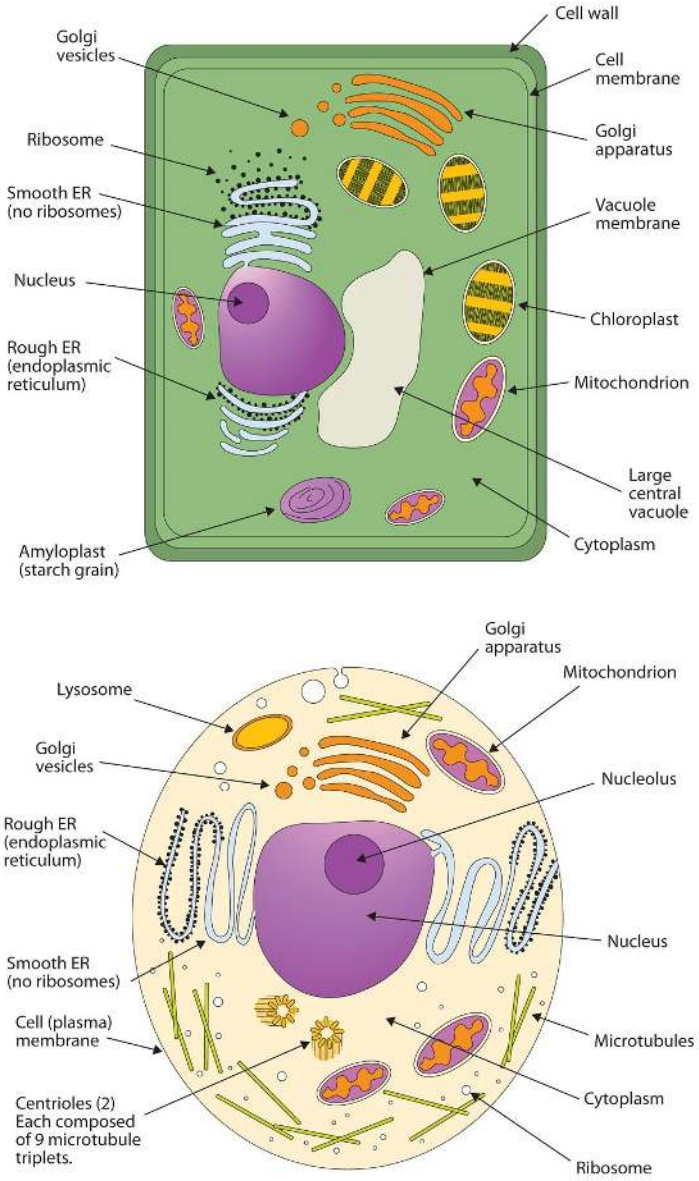


Figure 12.2.2.1: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

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 12.2.2.2).

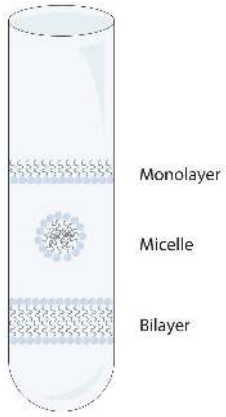


Figure 12.2.2.2: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

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 12.2.2.3).

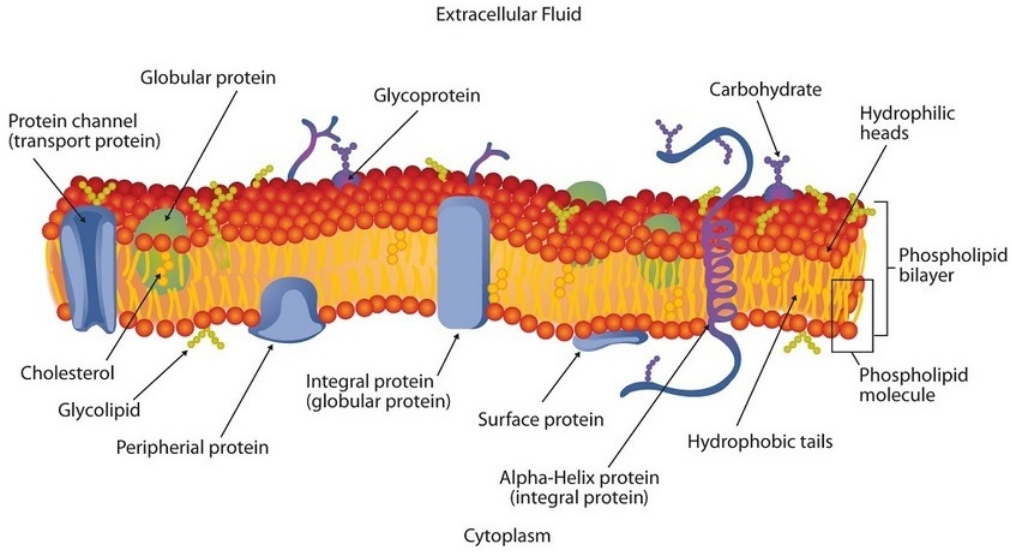


Figure 12.2.2.3: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

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 12.2.2.4.

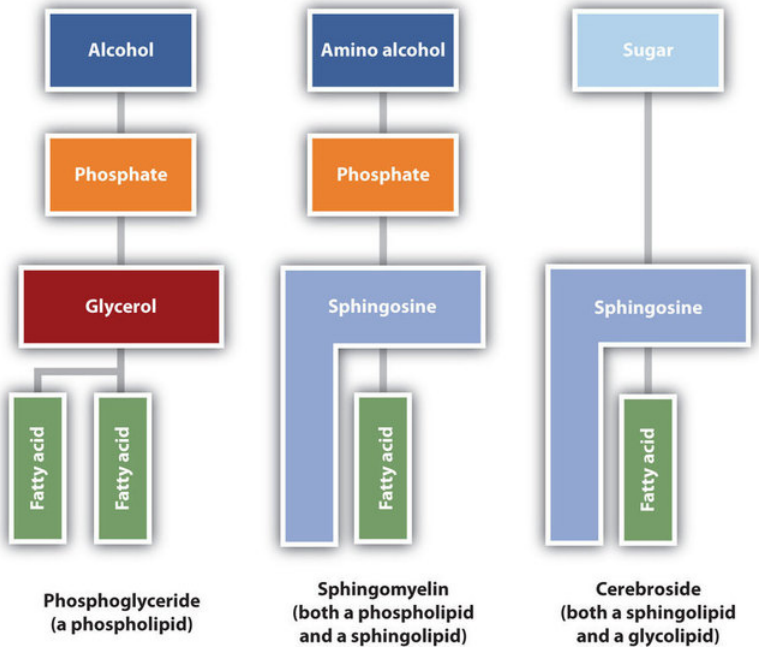


Figure 12.2.2.4: Component Structures of Some Important Membrane Lipids

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 12.2.2.5) is attached to the third carbon atom of glycerol (part (b) of Figure 12.2.2.5). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure 12.2.2.5).

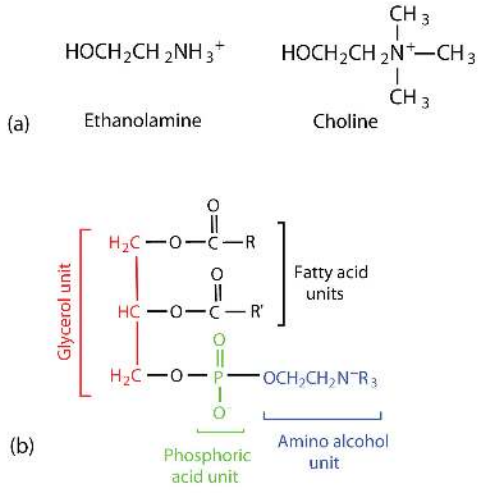
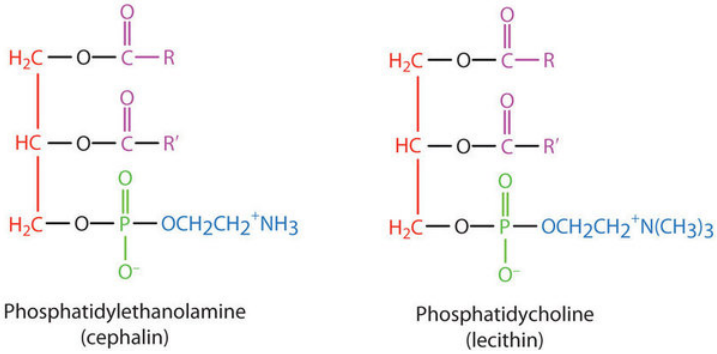


Figure 12.2.2.5: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

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 12.2.2.6). 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.

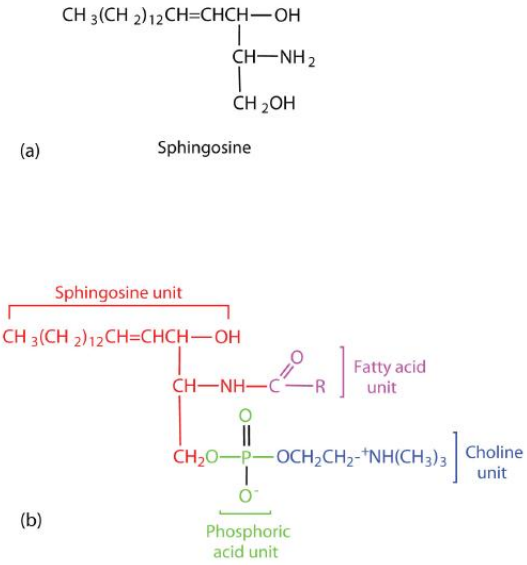


Figure 12.2.2.6: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.

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 12.2.2.7). 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.

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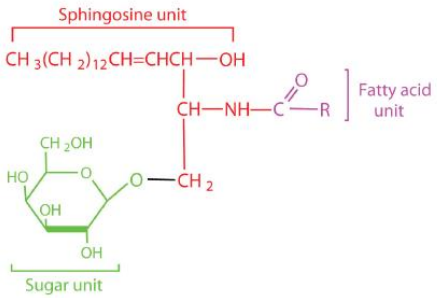


Figure 12.2.2.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.
General structure of a cerebroside with its sugar unit, sphingosine unit, and fatty acid unit highlighted in different colors.

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 12.2.2.3). 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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12.2.3: 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).

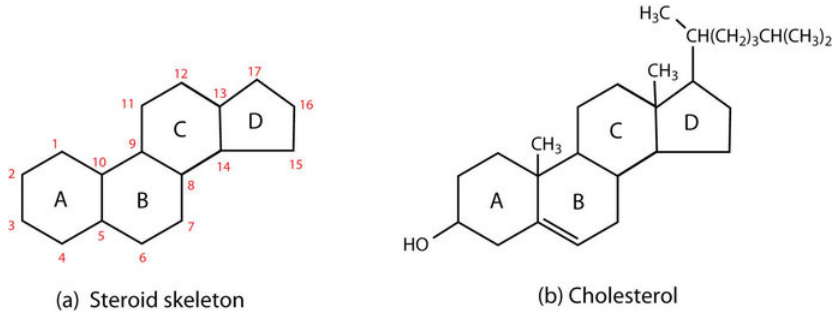


Figure 12.2.3.1 Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

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 12.2.3.1*a*. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure 12.2.3.1*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 12.2.3.2). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



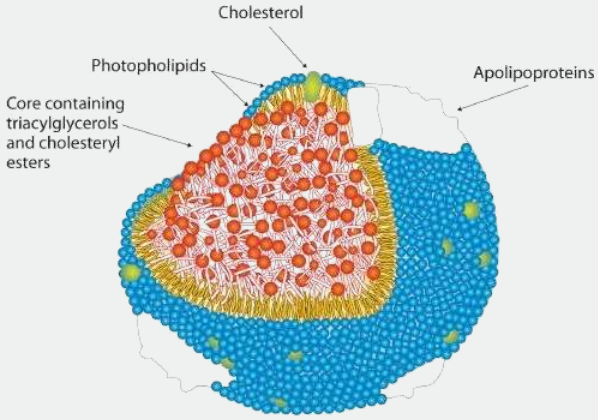
Figure 12.2.3.2: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

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.

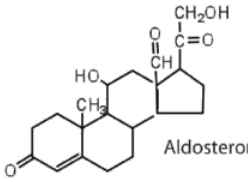
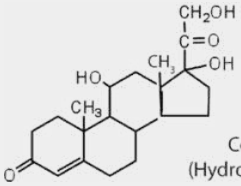
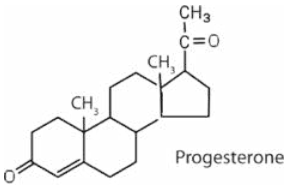
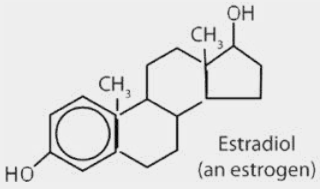
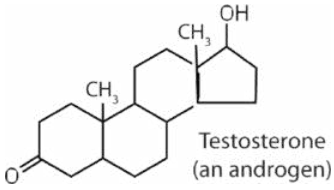
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount 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 12.2.3.1), 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 12.2.3.1: 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 12.2.3.3) and an amine such as the amino acid glycine (part (b) of Figure 12.2.3.3). 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.

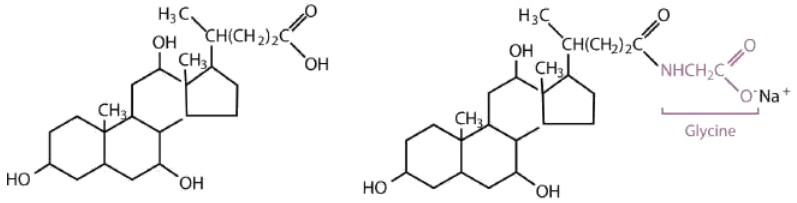


Figure 12.2.3.3 Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

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.

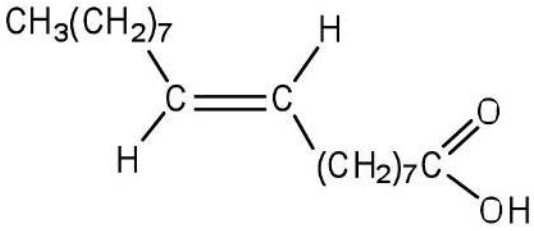
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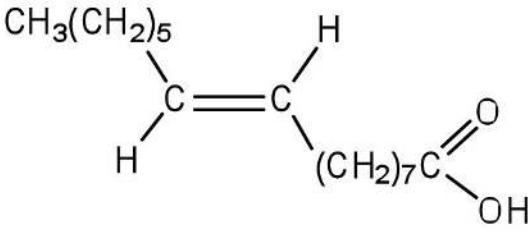
12.2.E: Exercises

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.

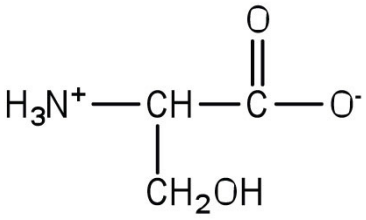


Elaidic acid



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.

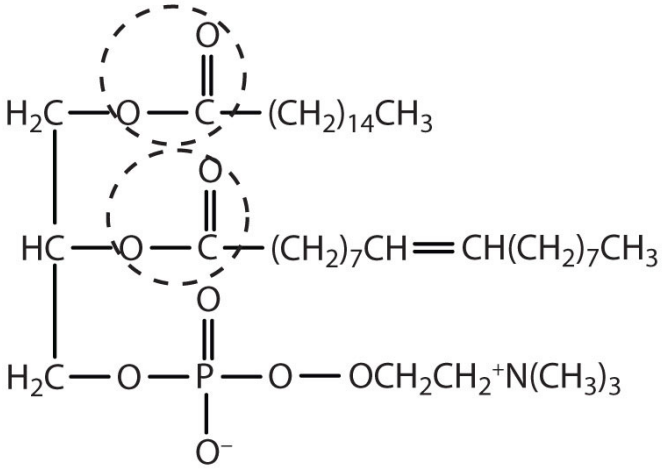


6. Explain whether each compound would be expected to diffuse through the lipid bilayer of a cell membrane.
   a. potassium chloride
   b. $CH_3CH_2CH_2CH_2CH_2CH_3$
   c. fructose
7. Identify the role of each steroid hormone in the body.
   a. progesterone
   b. aldosterone
   c. testosterone
   d. 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?

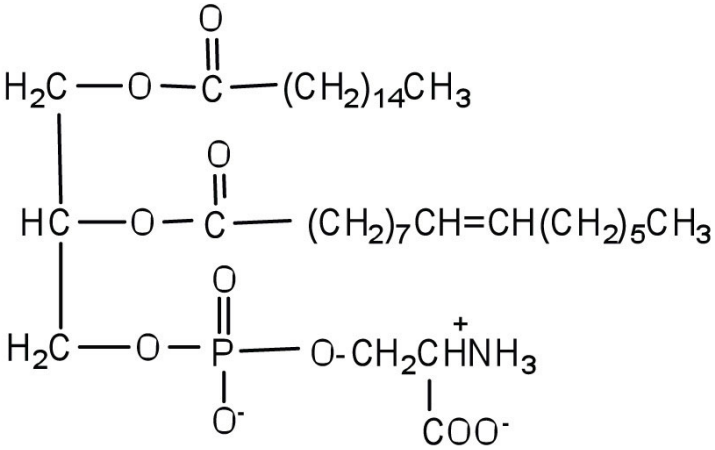
Answers

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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12.3: Amino Acids and Proteins

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 12.3.1: 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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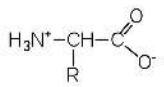
12.3.0: Properties of Amino Acids

Learning Objectives

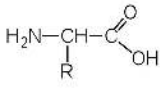
- To recognize amino acids and classify them based on the characteristics of their side chains.

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

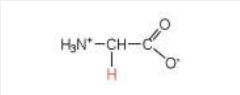
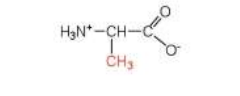
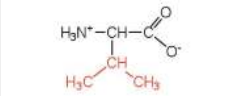
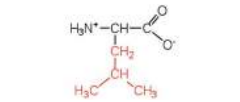
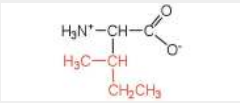
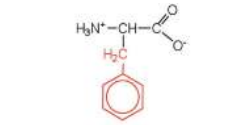
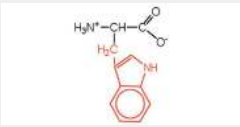
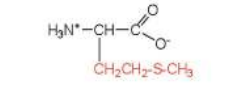
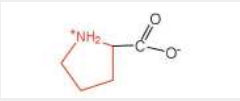
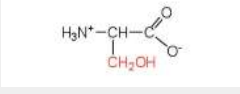
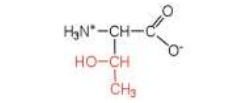
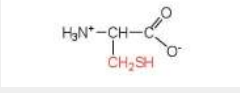


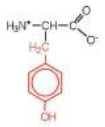
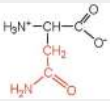
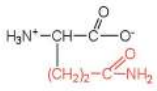
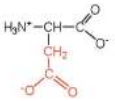
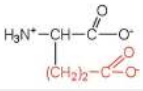
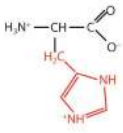
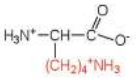
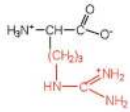
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

Classification

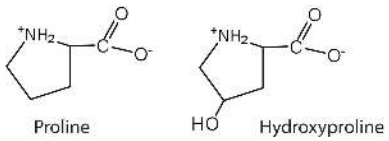
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound 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 12.3.0.1.

Table 12.3.0.1: 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*

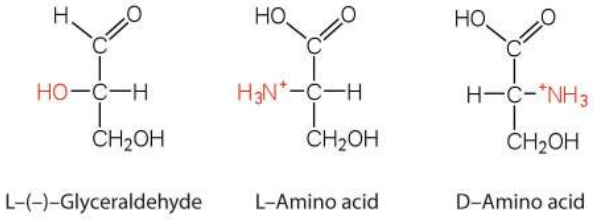
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic 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 12.3.0.1 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.

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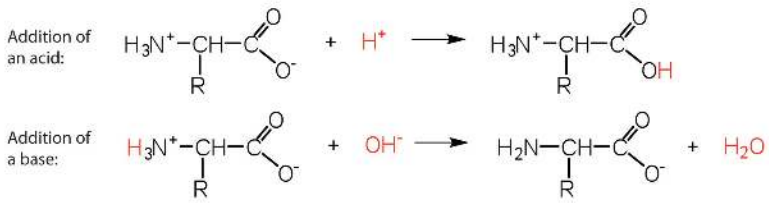
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12.3.1: Reactions of Amino Acids

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.

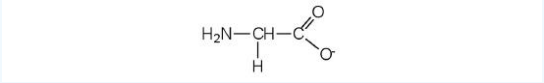


Example 12.3.1.1

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.



- The acid adds H^+ to the carboxylate group.



Exercise 12.3.1.1

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 12.3.1.1).

Table 12.3.1.1: ExampIes of Some Representative Amino Acids

Amino Acid	Classification	pI
alanine	nonpolar	6.0
valine	nonpolar	6.0
serine	polar, uncharged	5.7
threonine	polar, uncharged	6.5
arginine	positively charged (basic)	10.8
histidine	positively charged (basic)	7.6
lysine	positively charged (basic)	9.8
aspartic acid	negatively charged (acidic)	3.0
glutamic acid	negatively charged (acidic)	3.2

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.



Ninhydrin



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).

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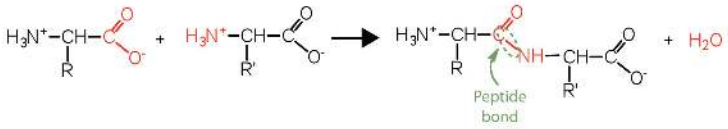
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12.3.2: Peptides

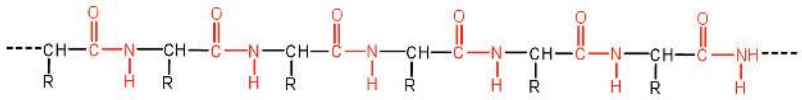
Learning Objectives

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

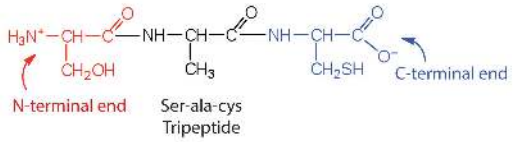
Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water 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.

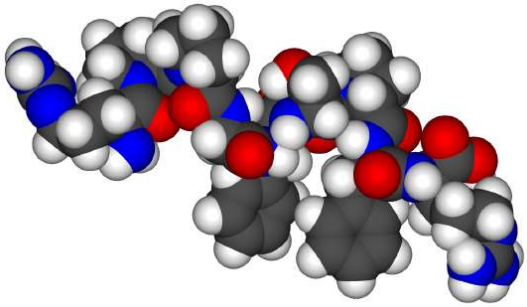


Figure 12.3.2.1: Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

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 12.3.2.1) 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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SECTION OVERVIEW

12.4: Nucleic Acids

The blueprint for the reproduction and the maintenance of each organism is found in the nuclei of its cells, concentrated in elongated, threadlike structures called chromosomes. These complex structures, consisting of DNA and proteins, contain the basic units of heredity, called genes. The number of chromosomes (and genes) varies with each species. Human body cells have 23 pairs of chromosomes having 20,000–40,000 different genes.

Sperm and egg cells contain only a single copy of each chromosome; that is, they contain only one member of each chromosome pair. Thus, in sexual reproduction, the entire complement of chromosomes is achieved only when an egg and sperm combine. A new individual receives half its hereditary material from each parent. Calling the unit of heredity a “gene” merely gives it a name. But what really are genes and how is the information they contain expressed? One definition of a gene is that it is a segment of DNA that constitutes the code for a specific polypeptide. If genes are segments of DNA, we need to learn more about the structure and physiological function of DNA. We begin by looking at the small molecules needed to form DNA and RNA (ribonucleic acid)—the nucleotides.

12.4.0: Nucleotides

12.4.1: Nucleic Acid Structure

12.4.E: Nucleic Acids (Exercises)

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12.4.0: Nucleotides

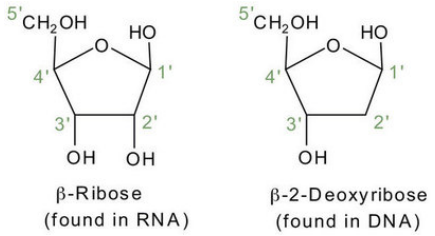
Learning Objectives

- To identify the different molecules that combine to form nucleotides.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a *ribonucleotide*, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a *deoxyribonucleotide*, and the nucleic acid is DNA.



The nitrogenous bases found in nucleotides are classified as pyrimidines or purines. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure 12.4.0.1).

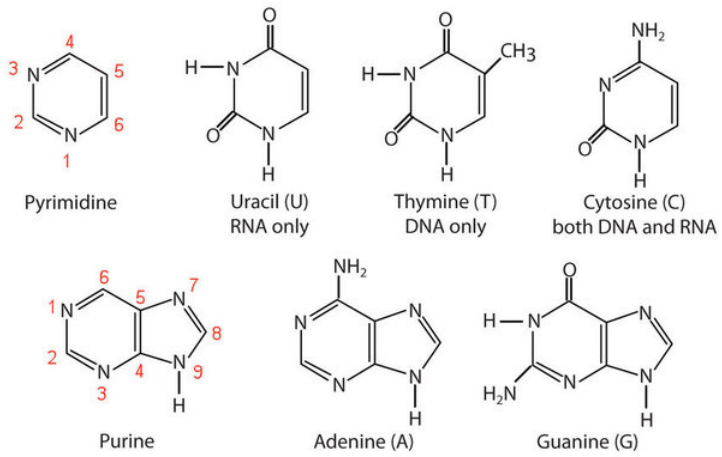


Figure 12.4.0.1: The Nitrogenous Bases Found in DNA and RNA

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table 12.4.0.1 summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

Table 12.4.0.1: Composition of Nucleotides in DNA and RNA

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure 12.4.0.2.

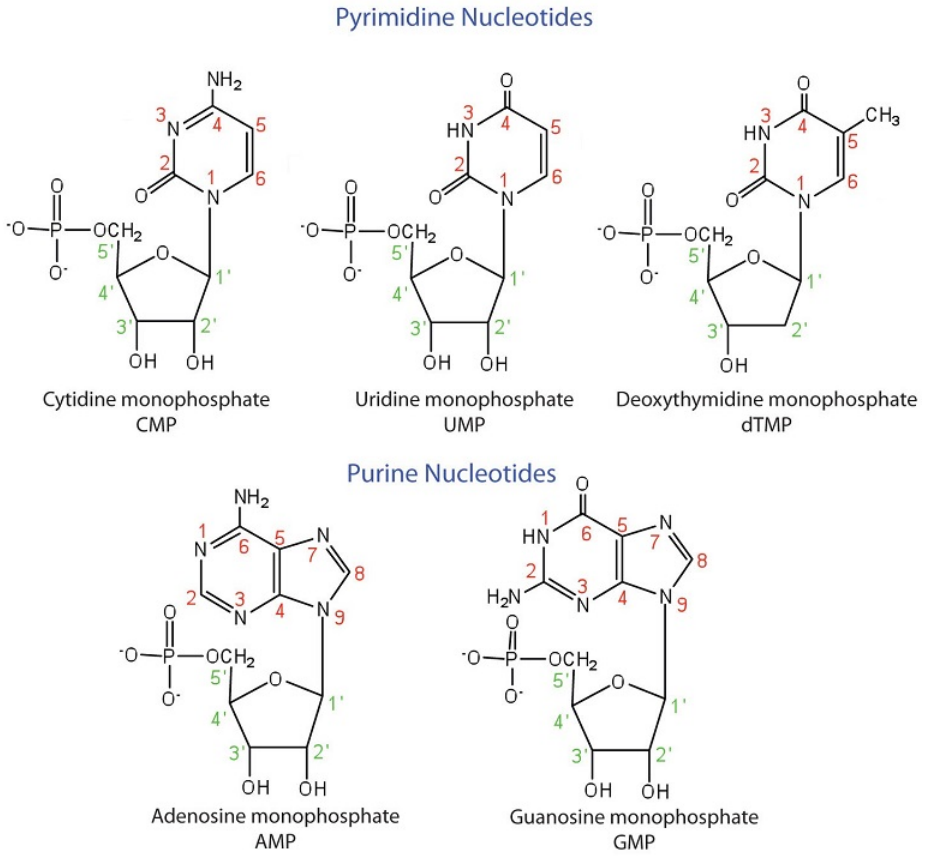


Figure 12.4.0.2: The Pyrimidine and Purine Nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure 12.4.0.3, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD^+), and coenzyme A, contain adenine nucleotides as structural components.

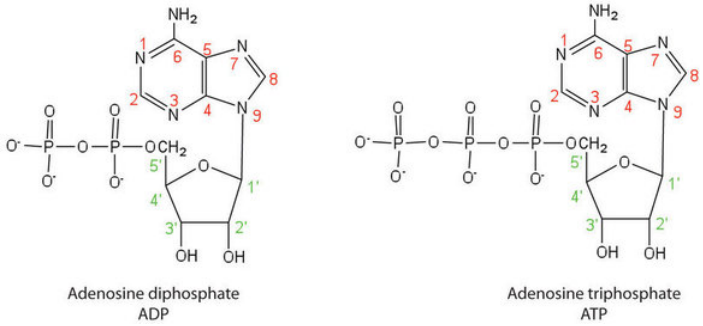


Figure 12.4.0.3: Structures of Two Important Adenine-Containing Nucleotides

Summary

Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.

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12.4.1: Nucleic Acid Structure

Skills to Develop

- Identify the two types of nucleic acids and the function of each type.
- Describe how nucleotides are linked together to form nucleic acids.
- Describe the secondary structure of DNA and the importance of complementary base pairing.

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure 12.4.1.1). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> *Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.*

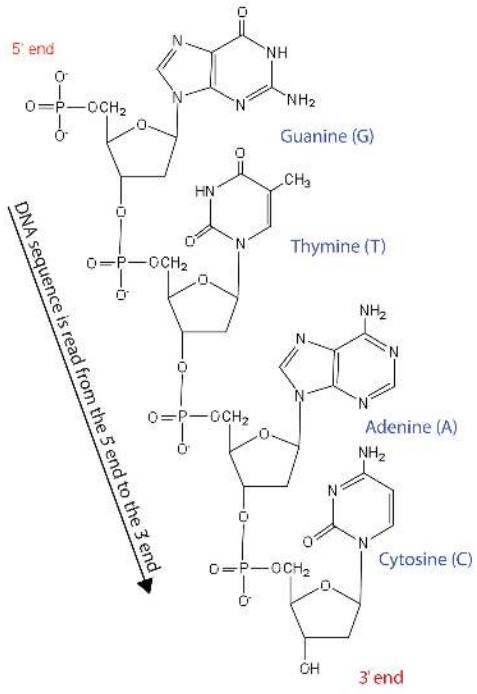


Figure 12.4.1.1 *Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2', and uracil would replace thymine.*

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases, shown in Figure 12.4.1.1) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are

deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure 12.4.1.1 would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure 12.4.1.2).

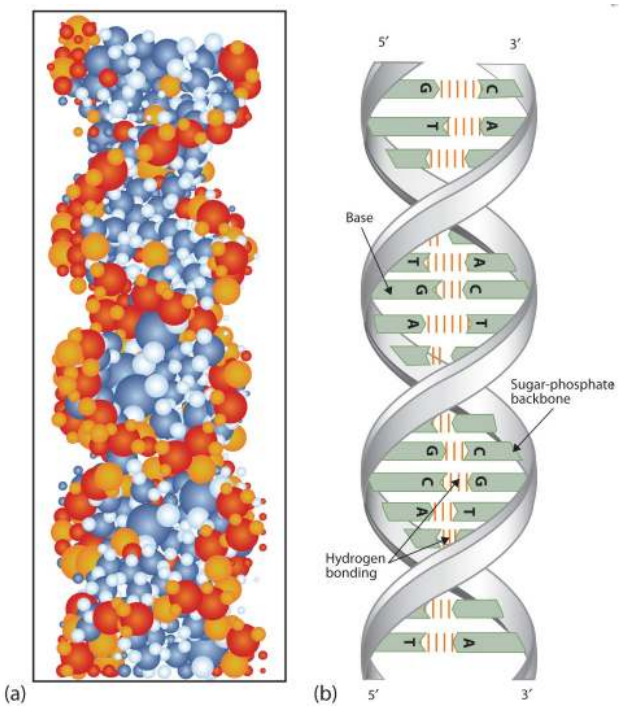


Figure 12.4.1.2 *DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.*

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure 12.4.1.3 shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

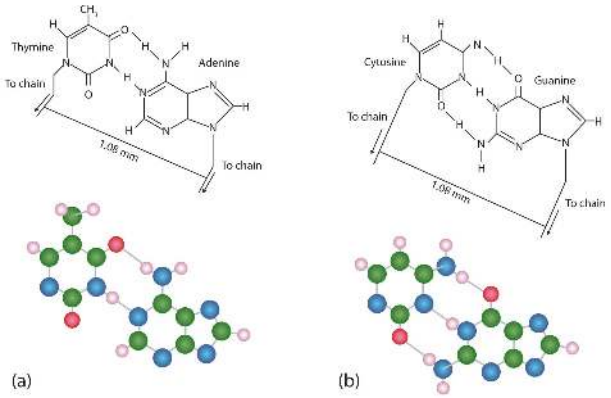


Figure 12.4.1.3 *Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.*

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure 12.4.1.4. If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure 12.4.1.3 is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

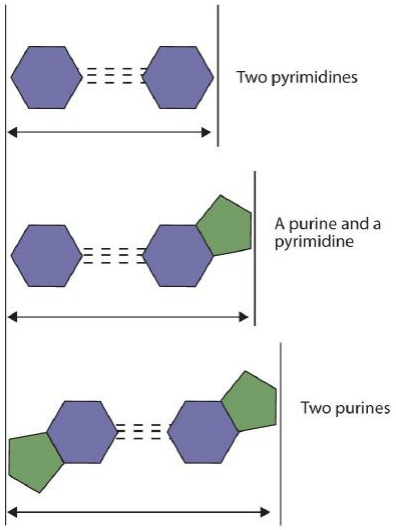


Figure 12.4.1.4 *Difference in Widths of Possible Base Pairs*

Summary

- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleotides are joined together to form nucleic acids through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.

Concept Review Exercises

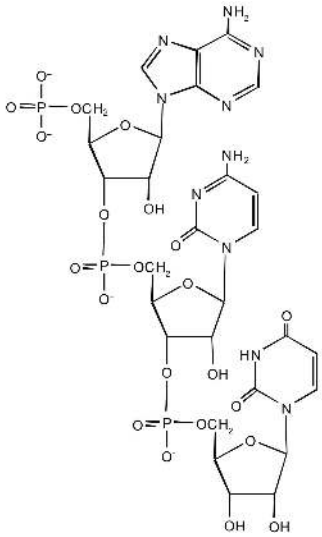
1.
   a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

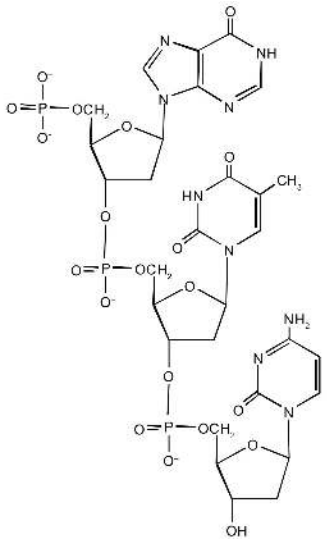
1.
   a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

Exercises

1. For this short RNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this DNA segment.



3. Which nitrogenous base in DNA pairs with each nitrogenous base?

   a. cytosine
   b. adenine
   c. guanine
   d. thymine

4. Which nitrogenous base in RNA pairs with each nitrogenous base?

   a. cytosine
   b. adenine
   c. guanine
   d. thymine

5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

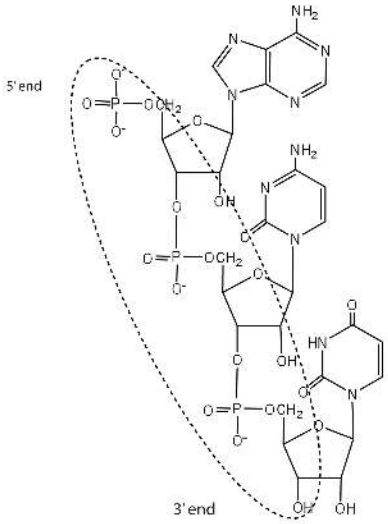
   5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′

6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

   5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

Answers

1.



c. ACU

3.

a. guanine
b. thymine
c. cytosine
d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

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12.4.E: Nucleic Acids (Exercises)

19.1: Nucleotides

Concept Review Exercises

1. Identify the three molecules needed to form the nucleotides in each nucleic acid.
   a. DNA
   b. RNA
2. Classify each compound as a pentose sugar, a purine, or a pyrimidine.
   a. adenine
   b. guanine
   c. deoxyribose
   d. thymine
   e. ribose
   f. cytosine

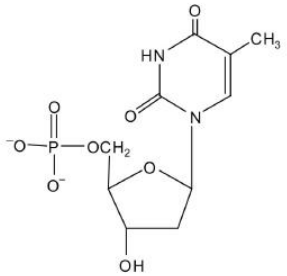
Answers

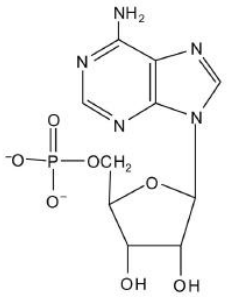
1. a. nitrogenous base (adenine, guanine, cytosine, and thymine), 2-deoxyribose, and H_3PO_4
   b. nitrogenous base (adenine, guanine, cytosine, and uracil), ribose, and H_3PO_4
2. a. purine
   b. purine
   c. pentose sugar
   d. pyrimidine
   e. pentose sugar
   f. pyrimidine

Exercises

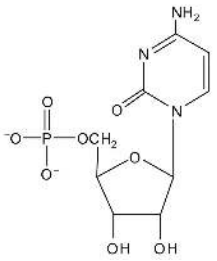
1. What is the sugar unit in each nucleic acid?
   a. RNA
   b. DNA
2. Identify the major nitrogenous bases in each nucleic acid.
   a. DNA
   b. RNA
3. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

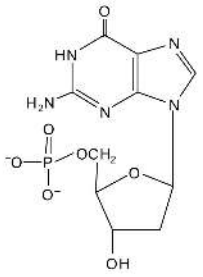
   a.



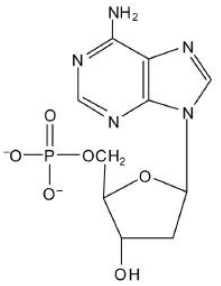
b. 

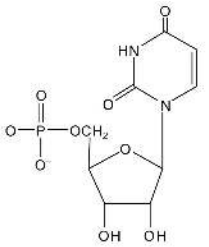
4. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

a. 

b. 

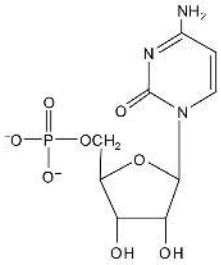
5. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a. 

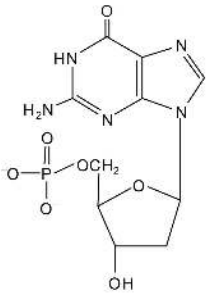
b. 

6. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a.



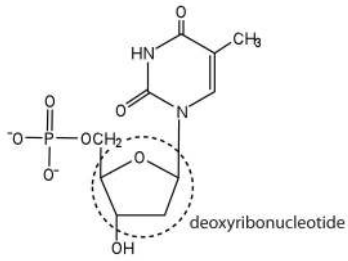
b.



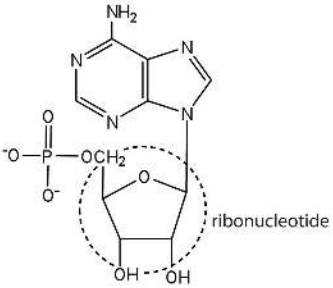
Answers

1. a. ribose
   b. deoxyribose

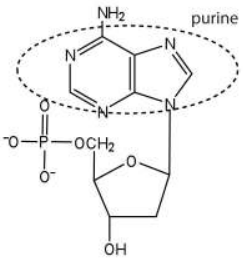
3. a.



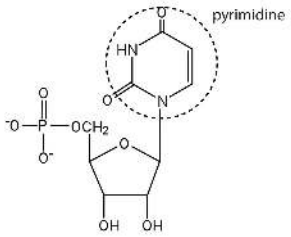
b.



a.



b.



19.2: Nucleic Acid Structure

Concept Review Exercises

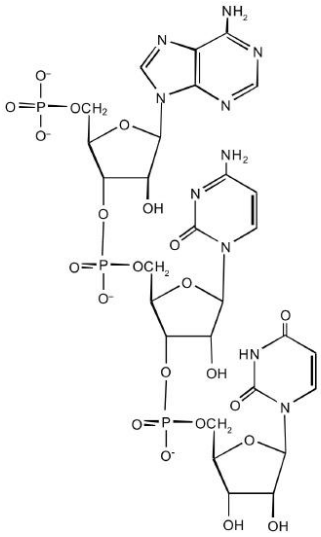
1. a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

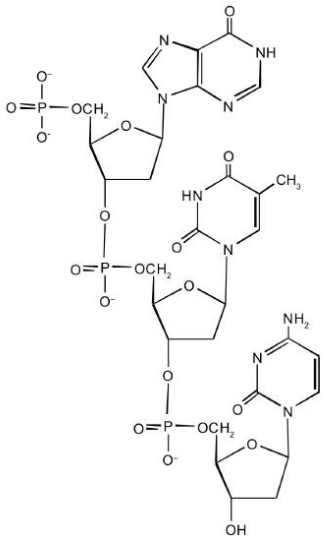
1. a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

Exercises

1. For this short RNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this DNA segment.

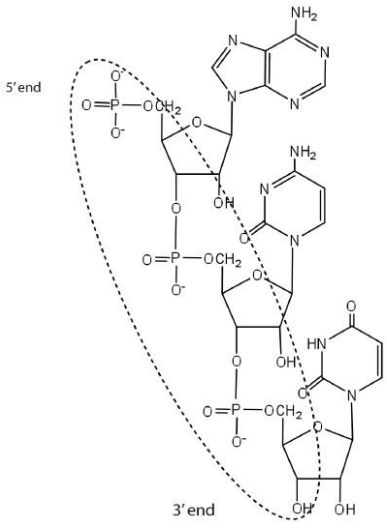


3. Which nitrogenous base in DNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′
6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

Answers

1. 

    c. ACU

3. a. guanine
   b. thymine
   c. cytosine
   d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

19.3: Replication and Expression of Genetic Information

Concept Review Exercises

1. In DNA replication, a parent DNA molecule produces two daughter molecules. What is the fate of each strand of the parent DNA double helix?
2. What is the role of DNA in transcription? What is produced in transcription?
3. Which type of RNA contains the codon? Which type of RNA contains the anticodon?

Answers

1. Each strand of the parent DNA double helix remains associated with the newly synthesized DNA strand.
2. DNA serves as a template for the synthesis of an RNA strand (the product of transcription).
3. codon: mRNA; anticodon: tRNA

Exercises

1. Describe how replication and transcription are similar.
2. Describe how replication and transcription differ.
3. A portion of the coding strand for a given gene has the sequence 5′-ATGAGCGACTTTGCGGGATTA-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?
4. A portion of the coding strand for a given gene has the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′.
   a. What is the sequence of complementary template strand?
   b. What is the sequence of the mRNA that would be produced during transcription from this segment of DNA?

Answers

1. Both processes require a template from which a complementary strand is synthesized.

3.

a. 3′-TACTCGCTGAAACGCCCTAAT-5′
b. 5′-AUGAGCGACUUUGCGGGAUUA-3′

19.4: Protein Synthesis and the Genetic Code

Concept Review Exercises

1. What are the roles of mRNA and tRNA in protein synthesis?
2. What is the initiation codon?
3. What are the termination codons and how are they recognized?

Answers

1. mRNA provides the code that determines the order of amino acids in the protein; tRNA transports the amino acids to the ribosome to incorporate into the growing protein chain.
2. AUG
3. UAA, UAG, and UGA; they are recognized by special proteins called release factors, which signal the end of the translation process.

Exercises

1. Write the anticodon on tRNA that would pair with each mRNA codon.
   a. 5′-UUU-3′
   b. 5′-CAU-3′
   c. 5′-AGC-3′
   d. 5′-CCG-3′
2. Write the codon on mRNA that would pair with each tRNA anticodon.
   a. 5′-UUG-3′
   b. 5′-GAA-3′
   c. 5′-UCC-3′
   d. 5′-CAC-3′
3. The peptide hormone oxytocin contains 9 amino acid units. What is the minimum number of nucleotides needed to code for this peptide?
4. Myoglobin, a protein that stores oxygen in muscle cells, has been purified from a number of organisms. The protein from a sperm whale is composed of 153 amino acid units. What is the minimum number of nucleotides that must be present in the mRNA that codes for this protein?
5. Use Figure 12.4.*E*.3 to identify the amino acids carried by each tRNA molecule in Exercise 1.
6. Use Figure 12.4.*E*.3 to identify the amino acids carried by each tRNA molecule in Exercise 2.
7. Use Figure 12.4.*E*.3 to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGAGCGACUUUGCGGGAUUA-3′.
8. Use Figure 12.4.*E*.3 to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGGCAAUCCUCAAACGCUGU-3′

Answers

1. a. 3′-AAA-5′
   b. 3′-GUA-5′
   c. 3′-UCG-5′
   d. 3′-GGC-5′
3. 27 nucleotides (3 nucleotides/codon)
5. 1a: phenyalanine; 1b: histidine; 1c: serine; 1d: proline
7. met-ser-asp-phe-ala-gly-leu

19.5: Mutations and Genetic Diseases

Concept Review Exercises

1. a. What effect can UV radiation have on DNA?
   b. Is UV radiation an example of a physical mutagen or a chemical mutagen?
2. a. What causes PKU?
   b. How is PKU detected and treated?

Answers

1. a. It can lead to the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer.
   b. physical mutagen
2. a. the absence of the enzyme phenylalanine hydroxylase
   b. PKU is diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites; treatment calls for an individual to be placed on a diet containing little or no phenylalanine.

Exercises

1. A portion of the coding strand of a gene was found to have the sequence 5′-ATGAGCGACTTTCGCCCATTA-3′. A mutation occurred in the gene, making the sequence 5′-ATGAGCGACCTTCGCCCATTA-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
2. A portion of the coding strand of a gene was found to have the sequence 5′-ATGGCAATCCTCAAACGCTGT-3′. A mutation occurred in the gene, making the sequence 5′-ATGGCAATCCTCAACGCTGT-3′.
   a. Identify the mutation as a substitution, an insertion, or a deletion.
   b. What effect would the mutation have on the amino acid sequence of the protein obtained from this mutated gene (use Figure 19.14)?
3. a. What is a mutagen?
   b. Give two examples of mutagens.
4. For each genetic disease, indicate which enzyme is lacking or defective and the characteristic symptoms of the disease.
   a. PKU
   b. Tay-Sachs disease

Answers

1. a. substitution
   b. Phenylalanine (UUU) would be replaced with leucine (CUU).
3. a. a chemical or physical agent that can cause a mutation
   b. UV radiation and gamma radiation (answers will vary)

19.6: Viruses

Questions

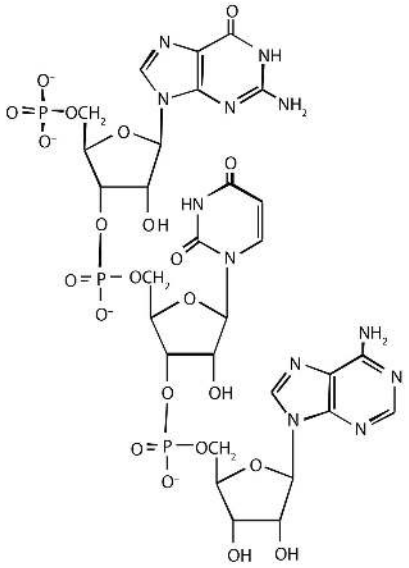
1. Describe the general structure of a virus.
2. How does a DNA virus differ from an RNA virus?
3. Why is HIV known as a retrovirus?
4. Describe how a DNA virus invades and destroys a cell.
5. a. Describe how an RNA virus invades and destroys a cell.
   b. How does this differ from a DNA virus?
6. What HIV enzyme does AZT inhibit?
7. What HIV enzyme does raltegravir inhibit?

Answers

1. A virus consists of a central core of nucleic acid enclosed in a protective shell of proteins. There may be lipid or carbohydrate molecules on the surface.
2. A DNA virus has DNA as its genetic material, while an RNA virus has RNA as its genetic material.
3. In a cell, a retrovirus synthesizes a DNA copy of its RNA genetic material.
4. The DNA virus enters a host cell and induces the cell to replicate the viral DNA and produce viral proteins. These proteins and DNA assemble into new viruses that are released by the host cell, which may die in the process.
5. -
6. reverse transcriptase
7. -

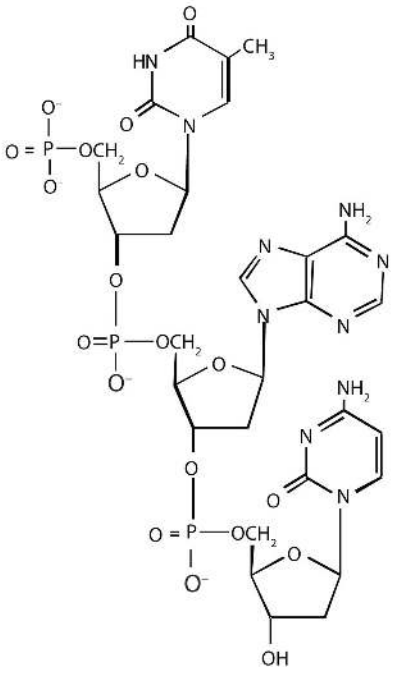
Additional Exercises

1. For this nucleic acid segment,



   a. classify this segment as RNA or DNA and justify your choice.
   b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

2. For this nucleic acid segment,



   a. classify this segment as RNA or DNA and justify your choice.
   b. determine the sequence of this segment, labeling the 5′ and 3′ ends.

3. One of the key pieces of information that Watson and Crick used in determining the secondary structure of DNA came from experiments done by E. Chargaff, in which he studied the nucleotide composition of DNA from many different species. Chargaff noted that the molar quantity of A was always approximately equal to the molar quantity of T, and the molar quantity of C was always approximately equal to the molar quantity of G. How were Chargaff's results explained by the structural model of DNA proposed by Watson and Crick?

4. Suppose Chargaff (see Exercise 3) had used RNA instead of DNA. Would his results have been the same; that is, would the molar quantity of A approximately equal the molar quantity of T? Explain.
5. In the DNA segment

   5′-ATGAGGCATGAGACG-3′ (coding strand) 3′-TACTCCGTACTCTGC-5′ (template strand)

   a. What products would be formed from the segment's replication?
   b. Write the mRNA sequence that would be obtained from the segment's transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 5b?
6. In the DNA segment

   5′-ATGACGGTTTACTAAGCC-3′ (coding strand) 3′-TACTGCCAAATGATTCGG-5′ (template strand)

   a. What products would be formed from the segment's replication?
   b. Write the mRNA sequence that would be obtained from the segment's transcription.
   c. What is the amino acid sequence of the peptide produced from the mRNA in Exercise 6b?
7. A hypothetical protein has a molar mass of 23,300 Da. Assume that the average molar mass of an amino acid is 120.

   a. How many amino acids are present in this hypothetical protein?
   b. What is the minimum number of codons present in the mRNA that codes for this protein?
   c. What is the minimum number of nucleotides needed to code for this protein?
8. Bradykinin is a potent peptide hormone composed of nine amino acids that lowers blood pressure.

   a. The amino acid sequence for bradykinin is arg-pro-pro-gly-phe-ser-pro-phe-arg. Postulate a base sequence in the mRNA that would direct the synthesis of this hormone. Include an initiation codon and a termination codon.
   b. What is the nucleotide sequence of the DNA that codes for this mRNA?
9. A particular DNA coding segment is ACGTTAGCCCCAGCT.

   a. Write the sequence of nucleotides in the corresponding mRNA.
   b. Determine the amino acid sequence formed from the mRNA in Exercise 9a during translation.
   c. What amino acid sequence results from each of the following mutations?

      a. replacement of the underlined guanine by adenine
      b. insertion of thymine immediately after the underlined guanine
      c. deletion of the underlined guanine
10. A particular DNA coding segment is TACGACGTAACAAGC.

    a. Write the sequence of nucleotides in the corresponding mRNA.
    b. Determine the amino acid sequence formed from the mRNA in Exercise 10a during translation.
    c. What amino acid sequence results from each of the following mutations?

       a. replacement of the underlined guanine by adenine
       b. replacement of the underlined adenine by thymine
11. Two possible point mutations are the substitution of lysine for leucine *or* the substitution of serine for threonine. Which is likely to be more serious and why?
12. Two possible point mutations are the substitution of valine for leucine *or* the substitution of glutamic acid for histidine. Which is likely to be more serious and why?

Answers

1.

   a. RNA; the sugar is ribose, rather than deoxyribose
   b. 5′-GUA-3′

3. In the DNA structure, because guanine (G) is always paired with cytosine (C) and adenine (A) is always paired with thymine (T), you would expect to have equal amounts of each.

5.

a. Each strand would be replicated, resulting in two double-stranded segments.
b. 5′-AUGAGGCAUGAGACG-3′
c. met-arg-his-glu-thr

7.

a. 194
b. 194
c. 582

9.

a. 5′-ACGUUAGCCCCAGCU-3′
b. thr-leu-ala-pro-ala
c.
   a. thr-leu-thr-pro-ala
   b. thr-leu-val-pro-ser
   c. thr-leu-pro-gin

11. substitution of lysine for leucine because you are changing from an amino acid with a nonpolar side chain to one that has a positively charged side chain; both serine and threonine, on the other hand, have polar side chains containing the OH group.

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CHAPTER OVERVIEW

13: Energy Metabolism

Metabolism is the set of life-sustaining chemical transformations within the cells of living organisms. The three main purposes of metabolism are the conversion of food/fuel to energy to run cellular processes, the conversion of food/fuel to building blocks for proteins, lipids, nucleic acids, and some carbohydrates, and the elimination of nitrogenous wastes. These enzyme-catalyzed reactions allow organisms to grow and reproduce, maintain their structures, and respond to their environments. Metabolism is usually divided into two categories: **catabolism**, the breaking down of organic matter, for example, by cellular respiration, and **anabolism**, the building up of components of cells such as proteins and nucleic acids. Usually, breaking down releases energy and building up consumes energy.

13.0: Prelude to Energy Metabolism
13.1: ATP- the Universal Energy Currency
13.2: Stage I of Catabolism
13.3: Overview of Stage II of Catabolism
13.4: Stage III of Catabolism
13.5: Stage II of Carbohydrate Catabolism
13.6: Stage II of Lipid Catabolism
13.7: Stage II of Protein Catabolism
13.E: Energy Metabolism (Exercises)
13.S: Energy Metabolism (Summary)

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13.0: Prelude to Energy Metabolism

The discovery of the link between insulin and diabetes led to a period of intense research aimed at understanding exactly how insulin works in the body to regulate glucose levels. Hormones in general act by binding to some protein, known as the hormone's receptor, thus initiating a series of events that lead to a desired outcome. In the early 1970s, the insulin receptor was purified, and researchers began to study what happens after insulin binds to its receptor and how those events are linked to the uptake and metabolism of glucose in cells.

The insulin receptor is located in the cell membrane and consists of four polypeptide chains: two identical chains called α chains and two identical chains called β chains. The α chains, positioned on the outer surface of the membrane, consist of 735 amino acids each and contain the binding site for insulin. The β chains are integral membrane proteins, each composed of 620 amino acids. The binding of insulin to its receptor stimulates the β chains to catalyze the addition of phosphate groups to the specific side chains of tyrosine (referred to as phosphorylation) in the β chains and other cell proteins, leading to the activation of reactions that metabolize glucose. In this chapter we will look at the pathway that breaks down glucose—in response to activation by insulin—for the purpose of providing energy for the cell.

GLmol

Figure 13.0.1: Model of the Structure of the Insulin Receptor (PDB code 4ZXB).

Life requires energy. Animals, for example, require heat energy to maintain body temperature, mechanical energy to move their limbs, and chemical energy to synthesize the compounds needed by their cells. Living cells remain organized and functioning properly only through a continual supply of energy. But only specific forms of energy can be used. Supplying a plant with energy by holding it in a flame will not prolong its life. On the other hand, a green plant is able to absorb radiant energy from the sun, the most abundant source of energy for life on the earth. Plants use this energy first to form glucose and then to make other carbohydrates, as well as lipids and proteins. Unlike plants, animals cannot directly use the sun's energy to synthesize new compounds. They must eat plants or other animals to get carbohydrates, fats, and proteins and the chemical energy stored in them. Once digested and transported to the cells, the nutrient molecules can be used in either of two ways: as building blocks for making new cell parts or repairing old ones or "burned" for energy.

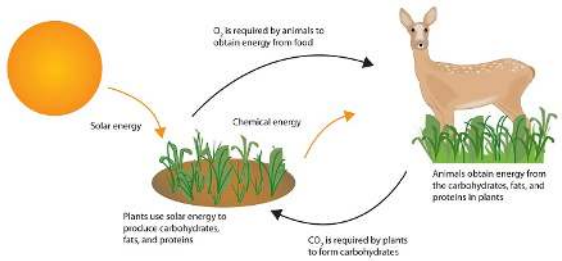


Figure 13.0.2: Some Energy Transformations in Living Systems. Plants and animals exist in a cycle; each requires products of the other.

The thousands of coordinated chemical reactions that keep cells alive are referred to collectively as **metabolism**. In general, metabolic reactions are divided into two classes: the breaking down of molecules to obtain energy is **catabolism**, and the building of new molecules needed by living systems is **anabolism**.

Definition: Metabolite

Any chemical compound that participates in a metabolic reaction is a *metabolite*.

Most of the energy required by animals is generated from lipids and carbohydrates. These fuels must be oxidized, or "burned," for the energy to be released. The oxidation process ultimately converts the lipid or carbohydrate to carbon dioxide (CO_2) and water (H_2O).

Carbohydrate:

$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + 670\,\text{kcal}$$

Lipid:

$$C_{16}H_{32}O_2 + 23\,O_2 \longrightarrow 16\,CO_2 + 16\,H_2O + 2{,}385\,\text{kcal}$$

These two equations summarize the biological combustion of a carbohydrate and a lipid by the cell through respiration. **Respiration** is the collective name for all metabolic processes in which gaseous oxygen is used to oxidize organic matter to carbon dioxide, water, and energy.

Like the combustion of the common fuels we burn in our homes and cars (wood, coal, gasoline), respiration uses oxygen from the air to break down complex organic substances to carbon dioxide and water. But the energy released in the burning of wood is manifested entirely in the form of heat, and excess heat energy is not only useless but also injurious to the living cell. Living organisms instead conserve much of the energy respiration releases by channeling it into a series of stepwise reactions that produce adenosine triphosphate (ATP) or other compounds that ultimately lead to the synthesis of ATP. The remainder of the energy is released as heat and manifested as body temperature.

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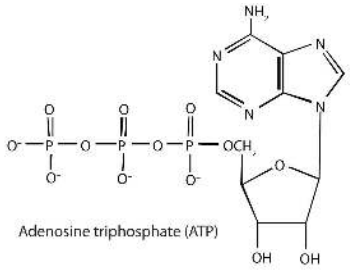
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13.1: ATP- the Universal Energy Currency

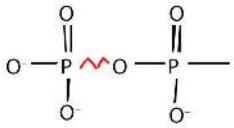
Learning Objectives

- To describe the importance of ATP as a source of energy in living organisms.

Adenosine triphosphate (ATP), a nucleotide composed of adenine, ribose, and three phosphate groups, is perhaps the most important of the so-called energy-rich compounds in a cell. Its concentration in the cell varies from 0.5 to 2.5 mg/mL of cell fluid.



Energy-rich compounds are substances having particular structural features that lead to a release of energy after hydrolysis. As a result, these compounds are able to supply energy for biochemical processes that require energy. The structural feature important in ATP is the phosphoric acid anhydride, or pyrophosphate, linkage:



The pyrophosphate bond, symbolized by a squiggle (~), is hydrolyzed when ATP is converted to adenosine diphosphate (ADP). In this hydrolysis reaction, the products contain less energy than the reactants; there is a release of energy (> 7 kcal/mol). One reason for the amount of energy released is that hydrolysis relieves the electron-electron repulsions experienced by the negatively charged phosphate groups when they are bonded to each other (Figure 20.1.1).

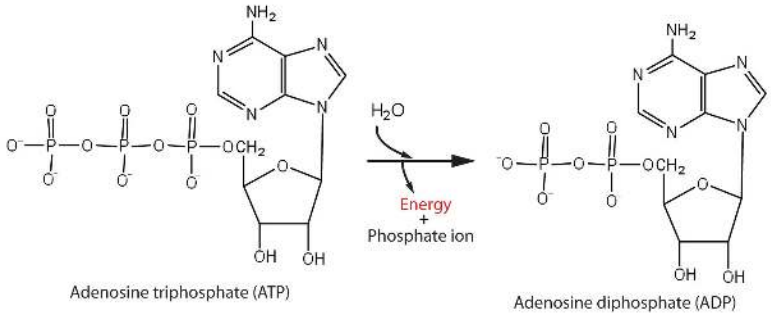


Figure 13.1.1: Hydrolysis of ATP to Form ADP

Energy is released because the products (ADP and phosphate ion) have less energy than the reactants [ATP and water (H_2O)].

The general equation for ATP hydrolysis is as follows:

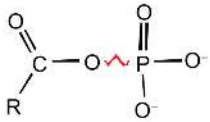
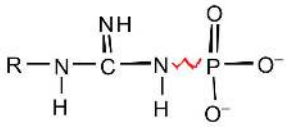
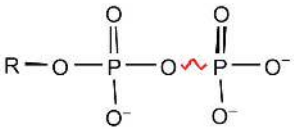
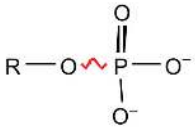
$$ATP + H_2O \rightarrow ADP + P_i + 7.4\ kcal/mol$$

If the hydrolysis of ATP releases energy, its synthesis (from ADP) requires energy. In the cell, ATP is produced by those processes that supply energy to the organism (absorption of radiant energy from the sun in green plants and breakdown of food in animals), and it is hydrolyzed by those processes that require energy (the syntheses of carbohydrates, lipids, proteins; the transmission of nerve impulses; muscle contractions). In fact, ATP is the principal medium of energy exchange in biological systems. Many scientists call it the energy currency of cells.

> *P_i is the symbol for the inorganic phosphate anions $H_2PO_4^-$ and HPO_4^{2-}.*

ATP is not the only high-energy compound needed for metabolism. Several others are listed in Table 13.1.1. Notice, however, that the energy released when ATP is hydrolyzed is approximately midway between those of the high-energy and the low-energy phosphate compounds. This means that the hydrolysis of ATP can provide energy for the phosphorylation of the compounds below it in the table. For example, the hydrolysis of ATP provides sufficient energy for the phosphorylation of glucose to form glucose 1-phosphate. By the same token, the hydrolysis of compounds, such as creatine phosphate, that appear *above* ATP in the table can provide the energy needed to resynthesize ATP from ADP.

Table 13.1.1: Energy Released by Hydrolysis of Some Phosphate Compounds

Type	Example	Energy Released (kcal/mol)
acyl phosphate 	1,3-bisphosphoglycerate (BPG)	−11.8
	acetyl phosphate	−11.3
guanidine phosphates 	creatine phosphate	−10.3
	arginine phosphate	−9.1
pyrophosphates 	$PP_{i*} \rightarrow 2P_i$	−7.8
	$ATP \rightarrow AMP + PP_i$	−7.7
	$ATP \rightarrow ADP + P_i$	−7.5
	$ADP \rightarrow AMP + P_i$	−7.5
sugar phosphates 	glucose 1-phosphate	−5.0
	fructose 6-phosphate	−3.8
	$AMP \rightarrow$ adenosine $+ P_i$	−3.4
	glucose 6-phosphate	−3.3
	glycerol 3-phosphate	−2.2

*PP_i is the pyrophosphate ion.

Summary

The hydrolysis of ATP releases energy that can be used for cellular processes that require energy.

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13.2: Stage I of Catabolism

Learning Objectives

- To describe how carbohydrates, fats, and proteins are broken down during digestion.

We have said that animals obtain chemical energy from the food—carbohydrates, fats, and proteins—they eat through reactions defined collectively as *catabolism*. We can think of catabolism as occurring in three stages (Figure 13.2.1). In stage I, carbohydrates, fats, and proteins are broken down into their individual monomer units: carbohydrates into simple sugars, fats into fatty acids and glycerol, and proteins into amino acids. One part of stage I of catabolism is the breakdown of food molecules by hydrolysis reactions into the individual monomer units—which occurs in the mouth, stomach, and small intestine—and is referred to as digestion.

In stage II, these monomer units (or building blocks) are further broken down through different reaction pathways, one of which produces ATP, to form a common end product that can then be used in stage III to produce even more ATP. In this chapter, we will look at each stage of catabolism—as an overview and in detail.

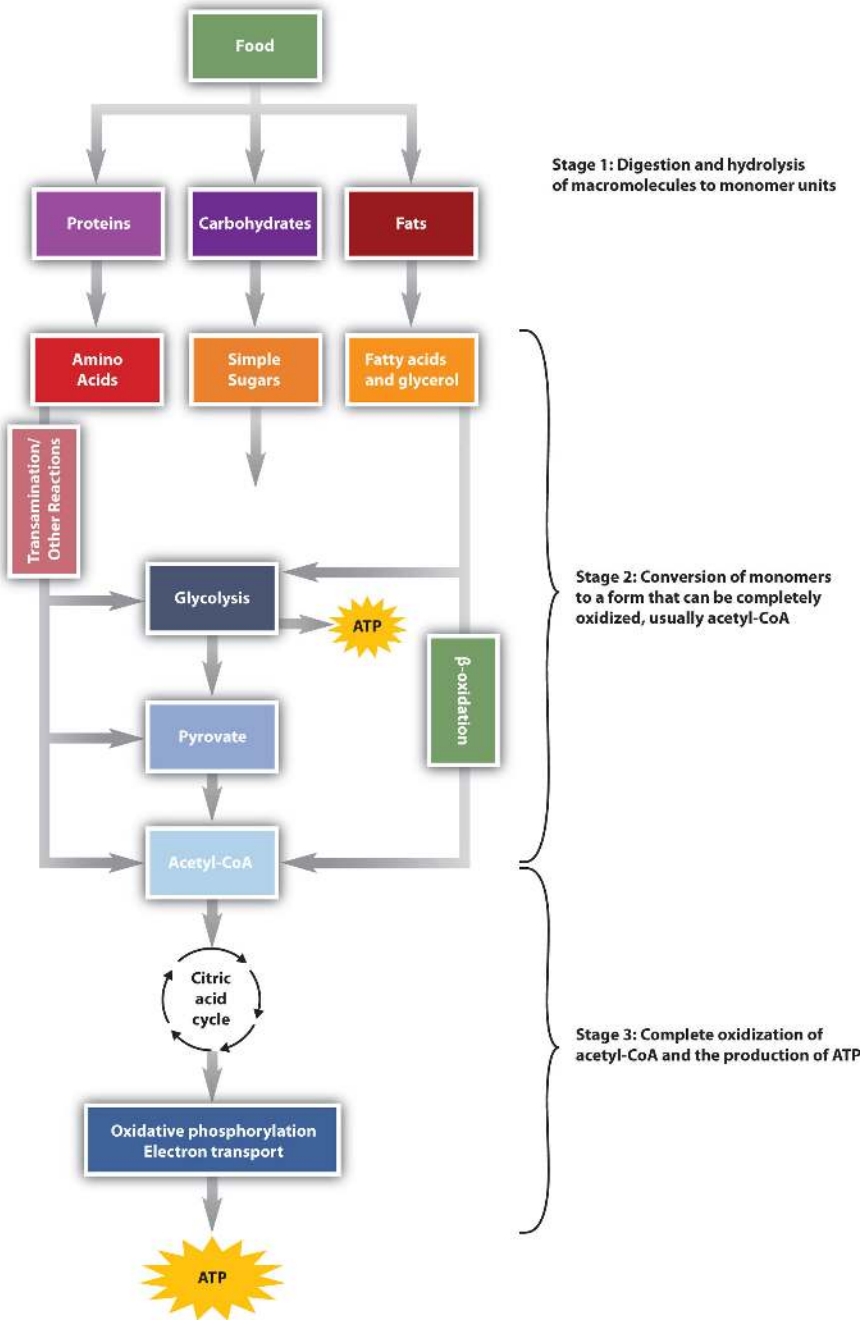


Figure 13.2.1: Energy Conversions

The conversion of food into cellular energy (as ATP) occurs in three stages.

Digestion of Carbohydrates

Carbohydrate digestion begins in the mouth (Figure 13.2.2) where salivary α-amylase attacks the α-glycosidic linkages in starch, the main carbohydrate ingested by humans. Cleavage of the glycosidic linkages produces a mixture of dextrins, maltose, and glucose. The α-amylase mixed into the food remains active as the food passes through the esophagus, but it is rapidly inactivated in the acidic environment of the stomach.

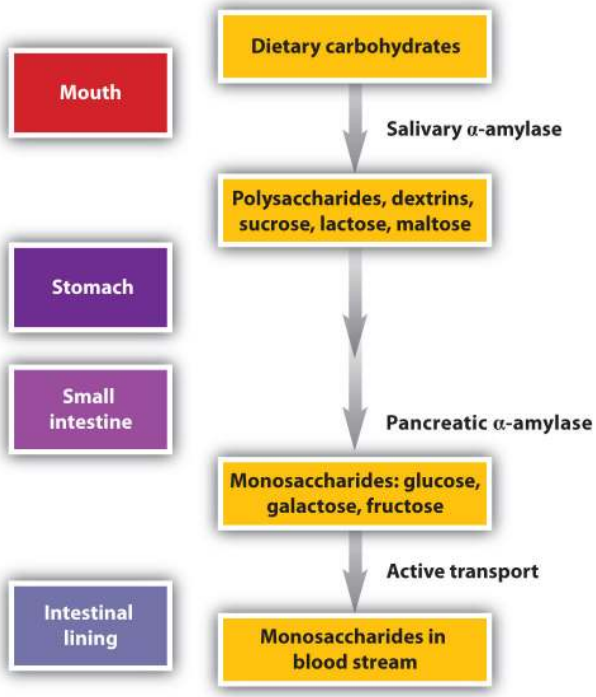


Figure 13.2.2: The Principal Events and Sites of Carbohydrate Digestion

The primary site of carbohydrate digestion is the small intestine. The secretion of α-amylase in the small intestine converts any remaining starch molecules, as well as the dextrins, to maltose. Maltose is then cleaved into two glucose molecules by maltase. Disaccharides such as sucrose and lactose are not digested until they reach the small intestine, where they are acted on by sucrase and lactase, respectively. The major products of the complete hydrolysis of disaccharides and polysaccharides are three monosaccharide units: glucose, fructose, and galactose. These are absorbed through the wall of the small intestine into the bloodstream.

Digestion of Proteins

Protein digestion begins in the stomach (Figure 13.2.3), where the action of gastric juice hydrolyzes about 10% of the peptide bonds. Gastric juice is a mixture of water (more than 99%), inorganic ions, hydrochloric acid, and various enzymes and other proteins.

> The pain of a gastric ulcer is at least partially due to irritation of the ulcerated tissue by acidic gastric juice.

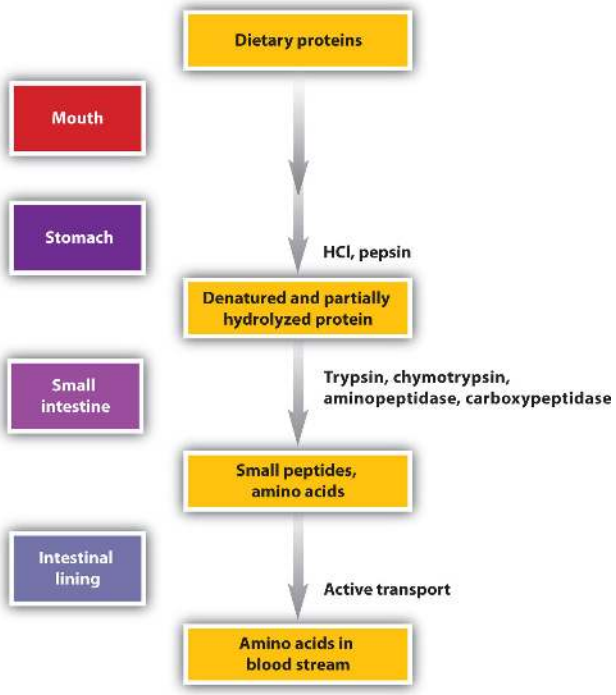


Figure 13.2.3: The Principal Events and Sites of Protein Digestion

The hydrochloric acid (HCl) in gastric juice is secreted by glands in the stomach lining. The pH of freshly secreted gastric juice is about 1.0, but the contents of the stomach may raise the pH to between 1.5 and 2.5. HCl helps to denature food proteins; that is, it unfolds the protein molecules to expose their chains to more efficient enzyme action. The principal digestive component of gastric juice is pepsinogen, an inactive enzyme produced in cells located in the stomach wall. When food enters the stomach after a period of fasting, pepsinogen is converted to its active form—pepsin—in a series of steps initiated by the drop in pH. Pepsin catalyzes the hydrolysis of peptide linkages within protein molecules. It has a fairly broad specificity but acts preferentially on linkages involving the aromatic amino acids tryptophan, tyrosine, and phenylalanine, as well as methionine and leucine.

Protein digestion is completed in the small intestine. Pancreatic juice, carried from the pancreas via the pancreatic duct, contains inactive enzymes such as trypsinogen and chymotrypsinogen. They are activated in the small intestine as follows (Figure 13.2.4): The intestinal mucosal cells secrete the proteolytic enzyme enteropeptidase, which converts trypsinogen to trypsin; trypsin then activates chymotrypsinogen to chymotrypsin (and also completes the activation of trypsinogen). Both of these active enzymes catalyze the hydrolysis of peptide bonds in protein chains. Chymotrypsin preferentially attacks peptide bonds involving the carboxyl groups of the aromatic amino acids (phenylalanine, tryptophan, and tyrosine). Trypsin attacks peptide bonds involving the carboxyl groups of the basic amino acids (lysine and arginine). Pancreatic juice also contains procarboxypeptidase, which is cleaved by trypsin to carboxypeptidase. The latter is an enzyme that catalyzes the hydrolysis of peptide linkages at the free carboxyl end of the peptide chain, resulting in the stepwise liberation of free amino acids from the carboxyl end of the polypeptide.

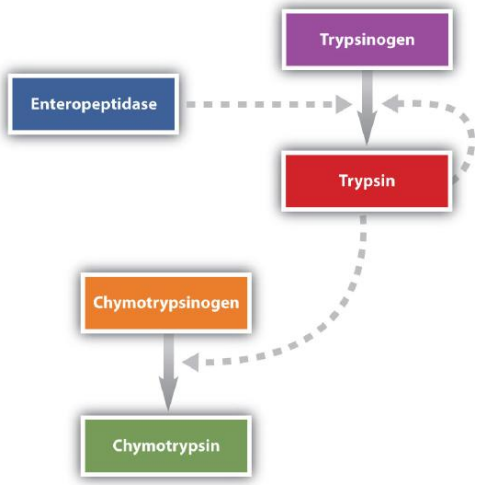


Figure 13.2.4: Activation of Some Pancreatic Enzymes in the Small Intestine

Aminopeptidases in the intestinal juice remove amino acids from the N-terminal end of peptides and proteins possessing a free amino group. Figure 13.2.5 illustrates the specificity of these protein-digesting enzymes. The amino acids that are released by protein digestion are absorbed across the intestinal wall into the circulatory system, where they can be used for protein synthesis.

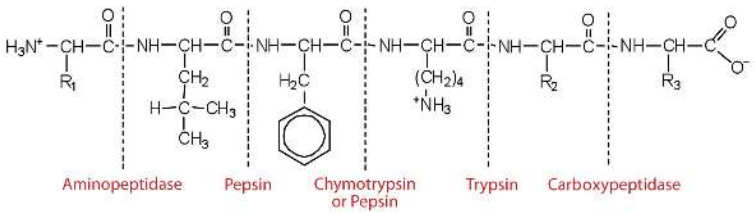


Figure 13.2.5: Hydrolysis of a Peptide by Several Peptidases

This diagram illustrates where in a peptide the different peptidases we have discussed would catalyze hydrolysis the peptide bonds.

Digestion of Lipids

Lipid digestion begins in the upper portion of the small intestine (Figure 13.2.6). A hormone secreted in this region stimulates the gallbladder to discharge bile into the duodenum. The principal constituents of bile are the bile salts, which emulsify large, water-insoluble lipid droplets, disrupting some of the hydrophobic interactions holding the lipid molecules together and suspending the resulting smaller globules (micelles) in the aqueous digestive medium. These changes greatly increase the surface area of the lipid particles, allowing for more intimate contact with the lipases and thus rapid digestion of the fats. Another hormone promotes the secretion of pancreatic juice, which contains these enzymes.

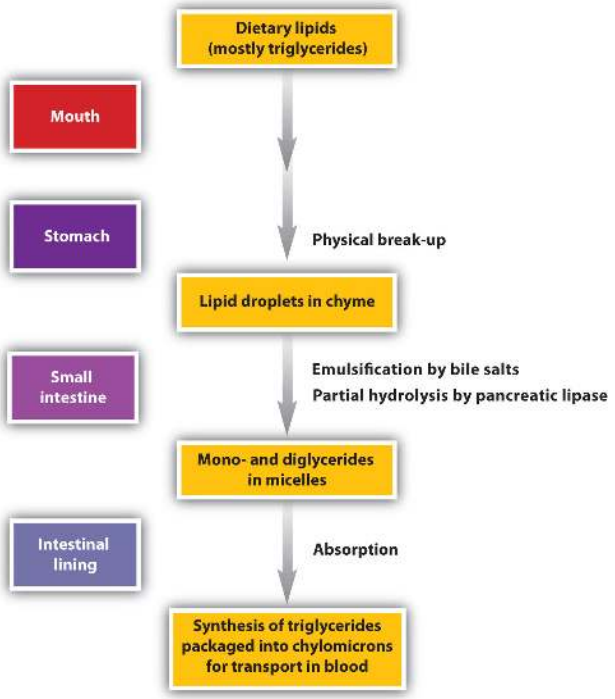
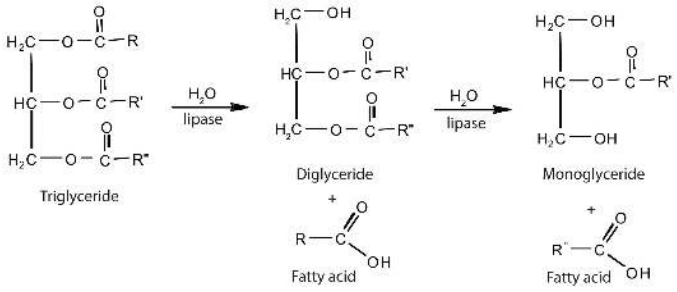


Figure 13.2.6: The Principal Events and Sites of Lipid (Primarily Triglyceride) Digestion

The lipases in pancreatic juice catalyze the digestion of triglycerides first to diglycerides and then to 2-monoglycerides and fatty acids:



The monoglycerides and fatty acids cross the intestinal lining into the bloodstream, where they are resynthesized into triglycerides and transported as lipoprotein complexes known as chylomicrons. Phospholipids and cholesteryl esters undergo similar hydrolysis in the small intestine, and their component molecules are also absorbed through the intestinal lining.

The further metabolism of monosaccharides, fatty acids, and amino acids released in stage I of catabolism occurs in stages II and III of catabolism.

Summary

During digestion, carbohydrates are broken down into monosaccharides, proteins are broken down into amino acids, and triglycerides are broken down into glycerol and fatty acids. Most of the digestion reactions occur in the small intestine.

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13.3: Overview of Stage II of Catabolism

Learning Objectives

- To describe the role of acetyl-CoA in metabolism.

A metabolic pathway is a series of biochemical reactions by which an organism converts a given reactant to a specific end product. There are specific metabolic pathways—which are different for carbohydrates, triglycerides, and proteins—that break down the products of stage I of catabolism (monosaccharides, fatty acids, and amino acids) to produce a common end product, acetyl-coenzyme A (acetyl-CoA) in stage II of catabolism.

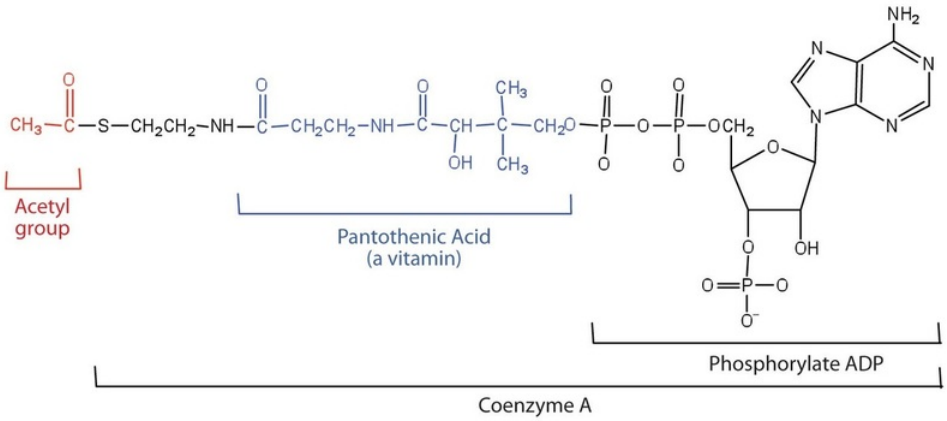


Figure 13.3.1: The Structure of Acetyl-Coenzyme A (Acetyl-CoA)

Acetyl-CoA is shown in Figure 13.3.1. The acetyl unit, derived (as we will see) from the breakdown of carbohydrates, lipids, and proteins, is attached to coenzyme A, making the acetyl unit more reactive. Acetyl-CoA is used in a myriad of biochemical pathways. For example, it may be used as the starting material for the biosynthesis of lipids (such as triglycerides, phospholipids, or cholesterol and other steroids). Most importantly for energy generation, it may enter the citric acid cycle and be oxidized to produce energy, if energy is needed and oxygen is available. The various fates or uses of acetyl-CoA are summarized in Figure 13.3.1.

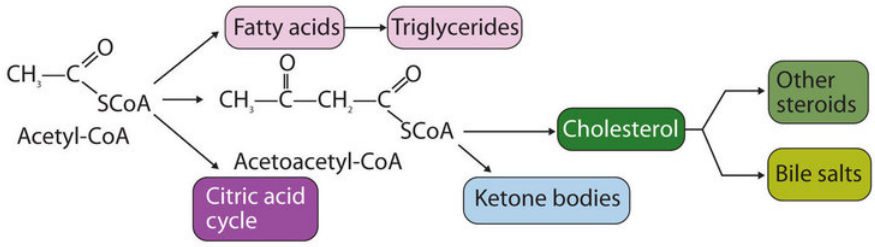


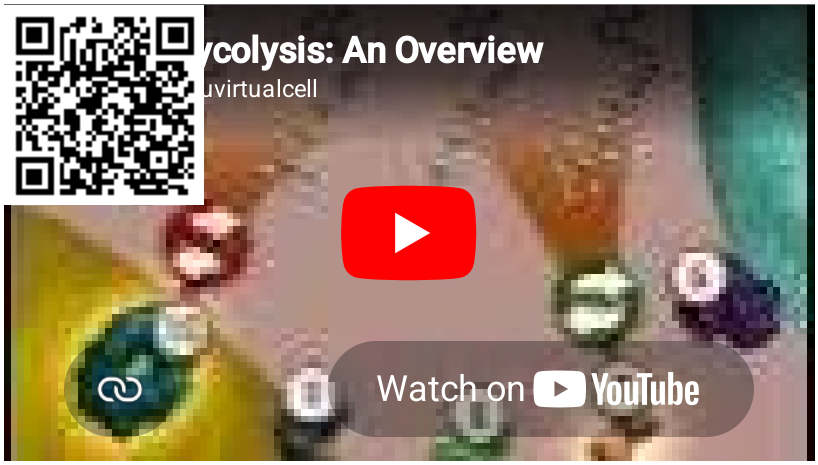
Figure 13.3.2: Cell Chemistry. Acetyl-CoA plays a variety of roles in cell chemistry.

Glycolysis

Glycolysis is the catabolic process in which glucose is converted into pyruvate via ten enzymatic steps. There are three regulatory steps, each of which is highly regulated that are separated into two phases:

1. the "priming phase" because it requires an input of energy in the form of 2 ATPs per glucose molecule and
2. the "pay off phase" because energy is released in the form of 4 ATPs, 2 per glyceraldehyde molecule.

The end result of Glycolysis is two new pyruvate molecules which can then be fed into the Citric Acid cycle (also known as the Kreb's Cycle) if oxygen is present, or can be reduced to lactate or ethanol in the absence of of oxygen using a process known as fermentation.



Video 13.3.1: Glycolysis: An Overview. Glycolysis is a series of 10 reactions that converts sugars, like glucose, into 3-carbon molecules called pyruvate. This animation provides an overview of the energy consumed and produced by the pathway. NDSU VCell Production's animation; for more information please see Vcell, NDSU(opens in new window) [vcell.ndsu.edu].

Glycolysis occurs within almost all living cells and is the primary source of Acetyl-CoA, which is the molecule responsible for the majority of energy output under aerobic conditions. The structures of Glycolysis intermediates can be found in Figure 13.3.3.

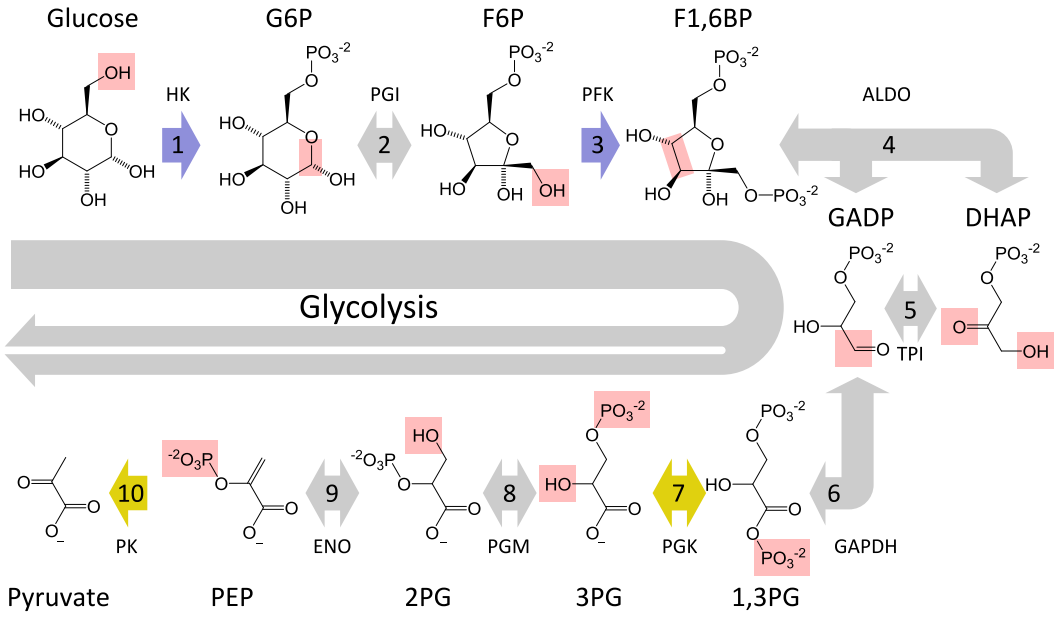


Figure 13.3.3: Glycolysis pathway. (CC BY-SA 4.0; International; Thomas Shafee via Wikipedia)

Phase 1: The "Priming Step"

The first phase of Glycolysis requires an input of energy in the form of ATP (adenosine triphosphate).

1. alpha-D-Glucose is phosphorolated at the 6 carbon by ATP via the enzyme Hexokinase (Class: Transferase) to yield alpha-D-Glucose-6-phosphate (G-6-P). This is a regulatory step which is negatively regulated by the presence of glucose-6-phosphate.
2. alpha-D-Glucose-6-phosphate is then converted into D-Fructose-6-phosphate (F-6-P) by Phosphoglucoisomerase (Class: Isomerase)
3. D-Fructose-6-phosphate is once again phosphorolated this time at the 1 carbon position by ATP via the enzyme Phosphofructokinase (Class: Transferase) to yield D-Fructose-1,6-bisphosphate (FBP). This is the committed step of glycolysis because of its large ΔG value.
4. D-Fructose-1,6-bisphosphate is then cleaved into two, three carbon molecules; Dihydroxyacetone phosphate (DHAP) and D-Glyceraldehyde-3-phosphate (G-3-P) by the enzyme Fructose bisphosphate aldolase (Class: Lyase)

5. Because the next portion of Glycolysis requires the molecule D-Glyceraldehyde-3-phosphate to continue Dihydroxyacetone phosphate is converted into D-Glyceraldehyde-3-phosphate by the enzyme Triose phosphate isomerase (Class: Isomerase)

Phase 2: The "Pay Off Step"

The second phase of Glycolysis where 4 molecules of ATP are produced per molecule of glucose. Enzymes appear in red:

1. D-Glyceraldehyde-3-phosphate is phosphorolated at the 1 carbon by the enzyme Glyceraldehyde-3-phosphate dehodrogenase to yield the high energy molecule 1,3-Bisphosphoglycerate (BPG)
2. ADP is then phosphorolated at the expense of 1,3-Bisphosphoglycerate by the enzyme Phosphoglycerate kinase (Class: Transferase) to yield ATP and 3-Phosphoglycerate (3-PG)
3. 3-Phosphoglycerate is then converted into 2-Phosphoglycerate by Phosphoglycerate mutase in preparation to yield another high energy molecule
4. 2-Phosphoglycerate is then converted to phosphoenolpyruvate (PEP) by Enolase. H_2O, potassium, and magnesium are all released as a result.
5. ADP is once again phosphorolated, this time at the expense of PEP by the enzyme pyruvate kinase to yield another molecule of ATP and and pyruvate. This step is regulated by the energy in the cell. The higher the energy of the cell the more inhibited pyruvate kinase becomes. Indicators of high energy levels within the cell are high concentrations of ATP, Acetyl-CoA, Alanine, and cAMP.

Because Glucose is split to yield two molecules of D-Glyceraldehyde-3-phosphate, each step in the "Pay Off" phase occurs twice per molecule of glucose.

Beta-Oxidation

The best source of energy for eukaryotic organisms are fats. Glucose offers a ratio 6.3 moles of ATP per carbon while saturated fatty acids offer 8.1 ATP per carbon. Also the complete oxidation of fats yields enormous amounts of water for those organisms that do not have adequate access to drinkable water. Camels and killer whales are good example of this, they obtain their water requirements from the complete oxidation of fats.



Video 13.3.2: Fatty acid metabolism / beta oxidation / β-Oxidation

There are four distinct stages in the oxidation of fatty acids. Fatty acid degradation takes place within the mitochondria and requires the help of several different enzymes. In order for fatty acids to enter the mitochondria the assistance of two carrier proteins is required, Carnitine acyltransferase I and II. It is also interesting to note the similarities between the four steps of beta-oxidation and the later four steps of the TCA cycle.

Entry into Beta-oxidation

Most fats stored in eukaryotic organisms are stored as triglycerides as seen below. In order to enter into beta-oxidation bonds must be broken usually with the use of a Lipase. The end result of these broken bonds are a glycerol molecule and three fatty acids in the case of triglycerides. Other lipids are capable of being degraded as well.

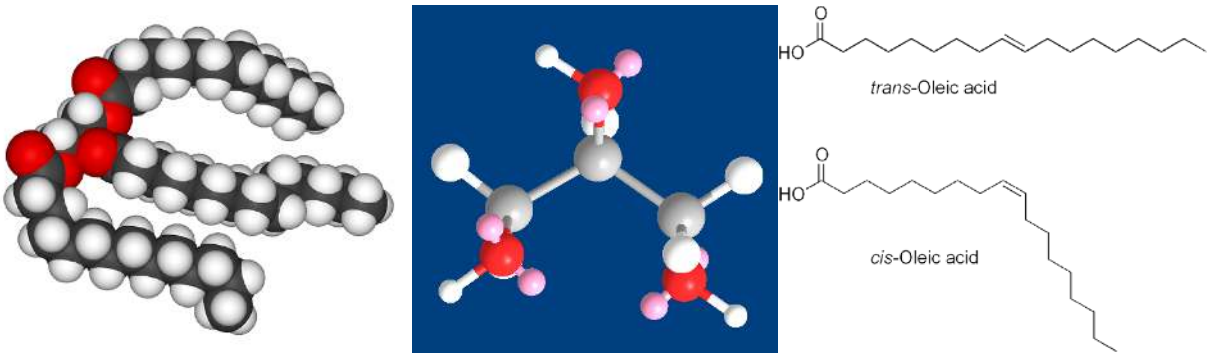


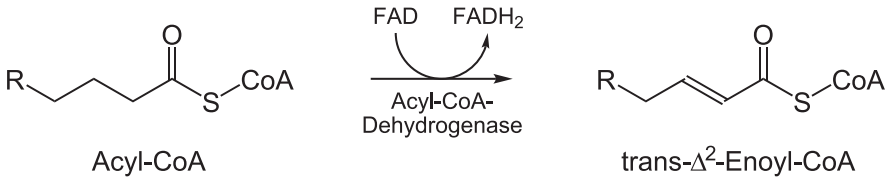
Figure 13.3.4: Key molecules in beta-oxidation: (left) A triglyceride molecule, (middle) Glycerol, (right) Fatty Acids (unsaturated)

Activation Step

- Once the triglycerides are broken down into glycerol and fatty acids they must be activated before they can enter into the mitochondria and proceed on with beta-oxidation. This is done by Acyl-CoA synthetase to yield fatty acyl-CoA.
- After the fatty acid has been acylated it is now ready to enter into the mitochondria.
- There are two carrier proteins (Carnitine acyltransferase I and II), one located on the outer membrane and one on the inner membrane of the mitochondria. Both are required for entry of the Acyl-CoA into the mitochondria.
- Once inside the mitochondria the fatty acyl-CoA can enter into beta-oxidation.

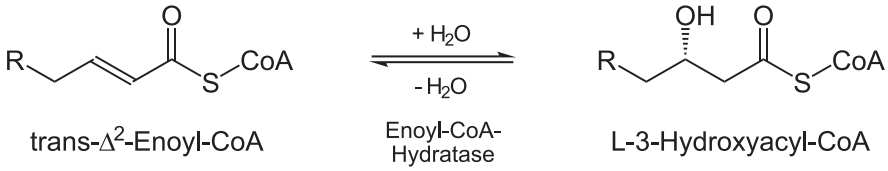
Oxidation Step

A fatty acyl-CoA is oxidized by Acyl-CoA dehydrogenase to yield a trans alkene. This is done with the aid of an [FAD] prosthetic group.



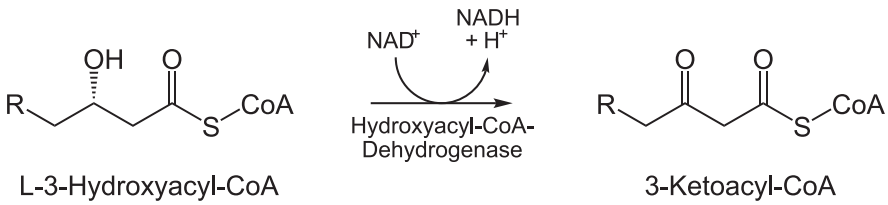
Hydration Step

The trans alkene is then hydrated with the help of Enoyl-CoA hydratase



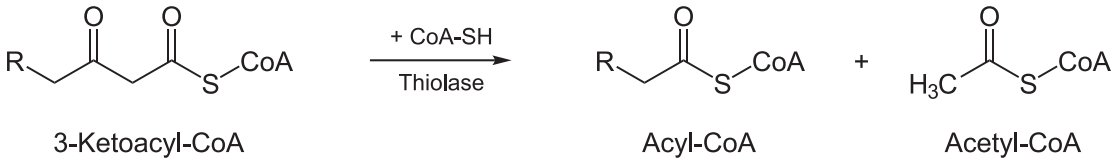
Oxidation Step

The alcohol of the hydroxyacly-CoA is then oxidized by NAD^+ to a carbonyl with the help of Hydroxyacyl-CoA dehydrogenase. NAD^+ is used to oxidize the alcohol rather then [FAD] because NAD^+ is capable of the alcohol while [FAD] is not.



Cleavage

Finally acetyl-CoA is cleaved off with the help of Thiolase to yield an Acyl-CoA that is two carbons shorter than before. The cleaved acetyl-CoA can then enter into the TCA and ETC because it is already within the mitochondria.



3-Ketoacyl-CoA | Acyl-CoA | Acetyl-CoA

Summary

Acetyl-CoA is formed from the breakdown of carbohydrates, lipids, and proteins. It is used in many biochemical pathways.

References

1. Garrett, H., Reginald and Charles Grisham. Biochemistry. Boston: Twayne Publishers, 2008.
2. Raven, Peter. Biology. Boston: Twayne Publishers, 2005.

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13.4: Stage III of Catabolism

Learning Objectives

- Describe the reactions of the citric acid cycle.
- Describe the function of the citric acid cycle and identify the products produced.
- Describe the role of the electron transport chain in energy metabolism.
- Describe the role of oxidative phosphorylation in energy metabolism.

The acetyl group enters a cyclic sequence of reactions known collectively as the citric acid cycle (or Krebs cycle or tricarboxylic acid [TCA] cycle). The cyclical design of this complex series of reactions, which bring about the oxidation of the acetyl group of acetyl-CoA to carbon dioxide and water, was first proposed by Hans Krebs in 1937. (He was awarded the 1953 Nobel Prize in Physiology or Medicine.) Acetyl-CoA's entrance into the citric acid cycle is the beginning of stage III of catabolism. The citric acid cycle produces adenosine triphosphate (ATP), reduced nicotinamide adenine dinucleotide (NADH), reduced flavin adenine dinucleotide ($FADH_2$), and metabolic intermediates for the synthesis of needed compounds.

Steps of the Citric Acid Cycle

At first glance, the citric acid cycle appears rather complex (Figure 13.4.1). All the reactions, however, are familiar types in organic chemistry: hydration, oxidation, decarboxylation, and hydrolysis. Each reaction of the citric acid cycle is numbered, and in Figure 13.4.1, the two acetyl carbon atoms are highlighted in red. Each intermediate in the cycle is a carboxylic acid, existing as an anion at physiological pH. All the reactions occur within the mitochondria, which are small organelles within the cells of plants and animals.

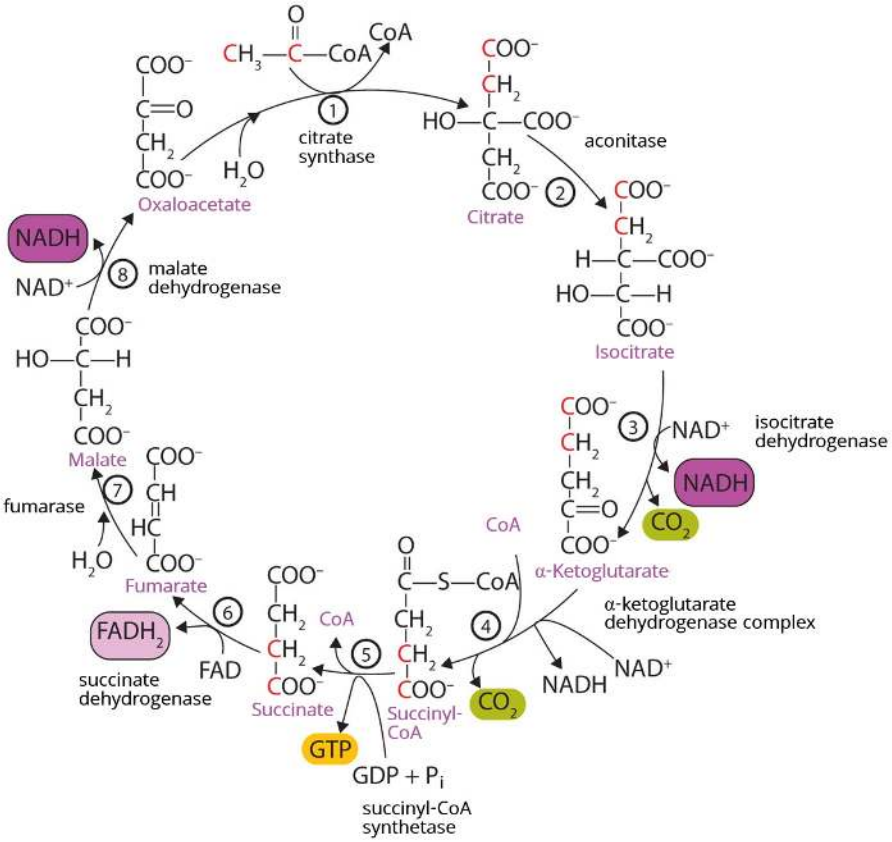


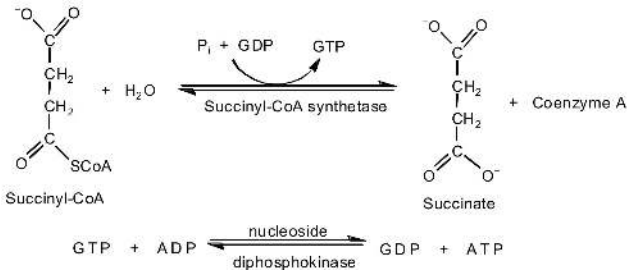
Figure 13.4.1: Reactions of the Citric Acid Cycle

1. In the first step, acetyl-CoA enters the citric acid cycle, and the acetyl group is transferred onto oxaloacetate, yielding citrate. Note that this step releases coenzyme A. The reaction is catalyzed by *citrate synthase*.

2. In the next step, *aconitase* catalyzes the isomerization of citrate to isocitrate. In this reaction, a tertiary alcohol, which cannot be oxidized, is converted to a secondary alcohol, which can be oxidized in the next step.
3. Isocitrate then undergoes a reaction known as oxidative decarboxylation because the alcohol is oxidized and the molecule is shortened by one carbon atom with the release of carbon dioxide (decarboxylation). The reaction is catalyzed by *isocitrate dehydrogenase*, and the product of the reaction is α-ketoglutarate. An important reaction linked to this is the reduction of the coenzyme nicotinamide adenine dinucleotide (NAD^+) to NADH. The NADH is ultimately reoxidized, and the energy released is used in the synthesis of ATP, as we shall see.
4. The fourth step is another oxidative decarboxylation. This time α-ketoglutarate is converted to succinyl-CoA, and another molecule of NAD^+ is reduced to NADH. The *α-ketoglutarate dehydrogenase complex* catalyzes this reaction. This is the only irreversible reaction in the citric acid cycle. As such, it prevents the cycle from operating in the reverse direction, in which acetyl-CoA would be synthesized from carbon dioxide.

> So far, in the first four steps, two carbon atoms have entered the cycle as an acetyl group, and two carbon atoms have been released as molecules of carbon dioxide. The remaining reactions of the citric acid cycle use the four carbon atoms of the succinyl group to resynthesize a molecule of oxaloacetate, which is the compound needed to combine with an incoming acetyl group and begin another round of the cycle.

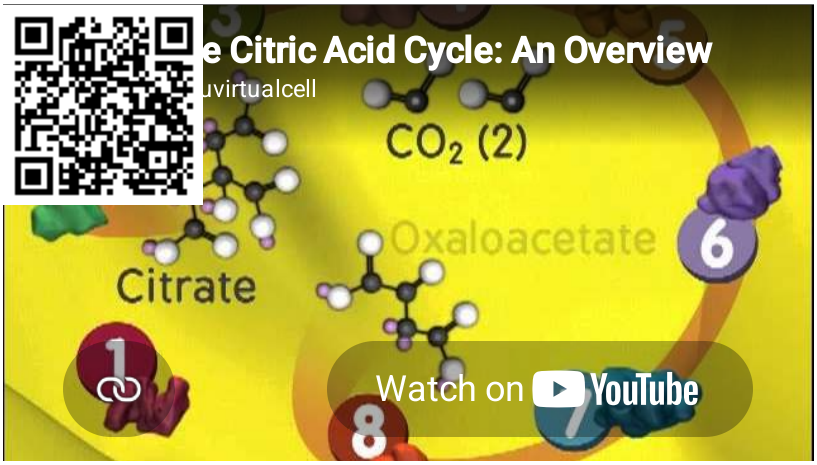
In the fifth reaction, the energy released by the hydrolysis of the high-energy thioester bond of succinyl-CoA is used to form guanosine triphosphate (GTP) from guanosine diphosphate (GDP) and inorganic phosphate in a reaction catalyzed by *succinyl-CoA synthetase*. This step is the only reaction in the citric acid cycle that directly forms a high-energy phosphate compound. GTP can readily transfer its terminal phosphate group to adenosine diphosphate (ADP) to generate ATP in the presence of *nucleoside diphosphokinase*.



Succinate dehydrogenase then catalyzes the removal of two hydrogen atoms from succinate, forming fumarate. This oxidation-reduction reaction uses flavin adenine dinucleotide (FAD), rather than NAD^+, as the oxidizing agent. Succinate dehydrogenase is the only enzyme of the citric acid cycle located within the inner mitochondrial membrane. We will see soon the importance of this.

In the following step, a molecule of water is added to the double bond of fumarate to form L-malate in a reaction catalyzed by *fumarase*.

One revolution of the cycle is completed with the oxidation of L-malate to oxaloacetate, brought about by *malate dehydrogenase*. This is the third oxidation-reduction reaction that uses NAD^+ as the oxidizing agent. Oxaloacetate can accept an acetyl group from acetyl-CoA, allowing the cycle to begin again.



Video: "The Citric Acid Cycle: An Overview". In the matrix of the mitochondrion, the Citric Acid Cycle uses Acetyl CoA molecules to produce energy through eight chemical reactions. This animation provides an overview of the pathway and its products. NDSU VCell Production's animation; for more information please see Vcell, NDSU, Animations(opens in new window) [vcell.ndsu.edu].

Cellular Respiration

Respiration can be defined as the process by which cells oxidize organic molecules in the presence of gaseous oxygen to produce carbon dioxide, water, and energy in the form of ATP. We have seen that two carbon atoms enter the citric acid cycle from acetyl-CoA (step 1), and two different carbon atoms exit the cycle as carbon dioxide (steps 3 and 4). Yet nowhere in our discussion of the citric acid cycle have we indicated how oxygen is used. Recall, however, that in the four oxidation-reduction steps occurring in the citric acid cycle, the coenzyme NAD^+ or FAD is reduced to NADH or $FADH_2$, respectively. *Oxygen is needed to reoxidize these coenzymes*. Recall, too, that very little ATP is obtained directly from the citric acid cycle. Instead, oxygen participation and significant ATP production occur subsequent to the citric acid cycle, in two pathways that are closely linked: electron transport and oxidative phosphorylation.

All the enzymes and coenzymes for the citric acid cycle, the reoxidation of NADH and $FADH_2$, and the production of ATP are located in the mitochondria, which are small, oval organelles with double membranes, often referred to as the “power plants” of the cell (Figure 13.4.2). A cell may contain 100–5,000 mitochondria, depending on its function, and the mitochondria can reproduce themselves if the energy requirements of the cell increase.

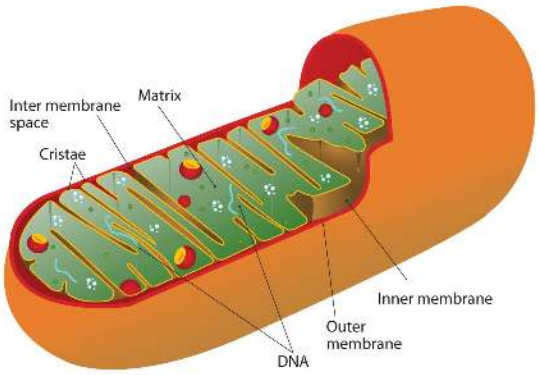


Figure 13.4.2: Respiration

Cellular respiration occurs in the mitochondria

Figure 13.4.2 shows the mitochondrion’s two membranes: *outer* and *inner*. The inner membrane is extensively folded into a series of internal ridges called *cristae*. Thus there are two compartments in mitochondria: the *intermembrane space*, which lies between the membranes, and the *matrix*, which lies inside the inner membrane. The outer membrane is permeable, whereas the inner membrane is impermeable to most molecules and ions, although water, oxygen, and carbon dioxide can freely penetrate both membranes. The matrix contains all the enzymes of the citric acid cycle with the exception of succinate dehydrogenase, which is

embedded in the inner membrane. The enzymes that are needed for the reoxidation of NADH and $FADH_2$ and ATP production are also located in the inner membrane. They are arranged in specific positions so that they function in a manner analogous to a bucket brigade. This highly organized sequence of oxidation-reduction enzymes is known as the electron transport chain (or respiratory chain).

Electron Transport

Figure 13.4.3 illustrates the organization of the electron transport chain. The components of the chain are organized into four complexes designated I, II, III, and IV. Each complex contains several enzymes, other proteins, and metal ions. The metal ions can be reduced and then oxidized repeatedly as electrons are passed from one component to the next. Recall that a compound is reduced when it gains electrons or hydrogen atoms and is oxidized when it loses electrons or hydrogen atoms.

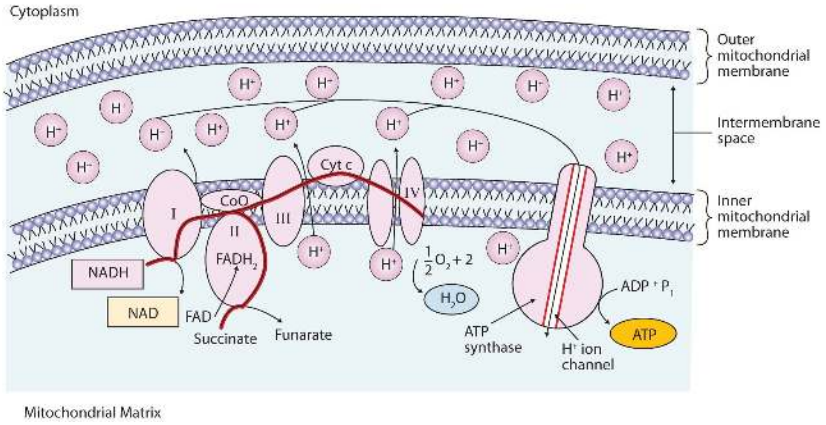
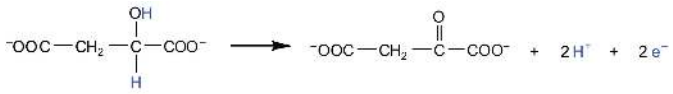


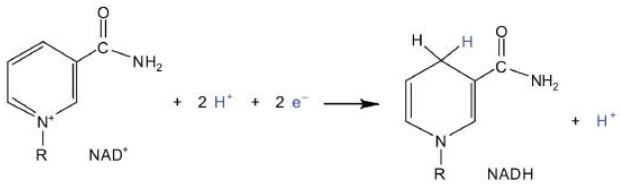
Figure 13.4.3: The Mitochondrial Electron Transport Chain and ATP Synthase. The red line shows the path of electrons.

Electrons can enter the electron transport chain through either complex I or II. We will look first at electrons entering at complex I. These electrons come from NADH, which is formed in three reactions of the citric acid cycle. Let's use step 8 as an example, the reaction in which L-malate is oxidized to oxaloacetate and NAD^+ is reduced to NADH. This reaction can be divided into two half reactions:

- *Oxidation half-reaction*:

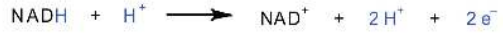


- *Reduction half-reaction*:

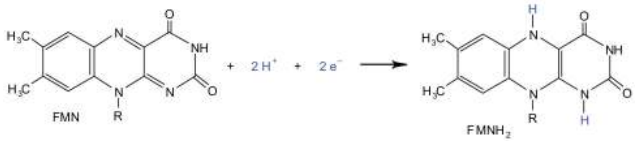


In the oxidation half-reaction, two hydrogen (H^+) ions and two electrons are removed from the substrate. In the reduction half-reaction, the NAD^+ molecule accepts both of those electrons and one of the H^+ ions. The other H^+ ion is transported from the matrix, across the inner mitochondrial membrane, and into the intermembrane space. The NADH diffuses through the matrix and is bound by complex I of the electron transport chain. In the complex, the coenzyme flavin mononucleotide (FMN) accepts both electrons from NADH. By passing the electrons along, NADH is oxidized back to NAD^+ and FMN is reduced to $FMNH_2$ (reduced form of flavin mononucleotide). Again, the reaction can be illustrated by dividing it into its respective half-reactions.

- *Oxidation half-reaction*:



- *Reduction half-reaction*:



Complex I contains several proteins that have iron-sulfur (Fe·S) centers. The electrons that reduced FMN to $FMNH_2$ are now transferred to these proteins. The iron ions in the Fe·S centers are in the Fe(III) form at first, but by accepting an electron, each ion is reduced to the Fe(II) form. Because each Fe·S center can transfer only one electron, two centers are needed to accept the two electrons that will regenerate FMN.

- *Oxidation half-reaction*:

$$\mathrm{FMNH_2 \longrightarrow FMN + 2\,H^+ + 2\,e^-}$$

- *Reduction half-reaction*:

$$\mathrm{2\,Fe(III)\ \cdot S + 2\,e^- \longrightarrow 2\,Fe(II)\ \cdot S}$$

Electrons from $FADH_2$, formed in step 6 of the citric acid cycle, enter the electron transport chain through complex II. Succinate dehydrogenase, the enzyme in the citric acid cycle that catalyzes the formation of $FADH_2$ from FAD is part of complex II. The electrons from $FADH_2$ are then transferred to an Fe·S protein.

- *Oxidation half-reaction*:

$$\mathrm{FADH_2 \longrightarrow FAD + 2\,H^+ + 2\,e^-}$$

- *Reduction half-reaction*:

$$\mathrm{2\,Fe(III)\ \cdot S + 2\,e^- \longrightarrow 2\,Fe(II)\ \cdot S}$$

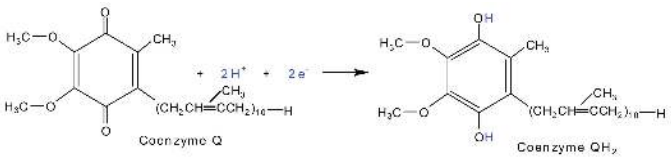
Electrons from complexes I and II are then transferred from the $\mathrm{Fe\ \cdot S}$ protein to coenzyme Q (CoQ), a mobile electron carrier that acts as the electron shuttle between complexes I or II and complex III.

> *Coenzyme Q is also called ubiquinone because it is ubiquitous in living systems.*

- *Oxidation half-reaction*:

$$\mathrm{2\,Fe(II)\ \cdot S \longrightarrow 2\,Fe(III)\ \cdot S + 2\,e^-}$$

- *Reduction half-reaction*:



Complexes III and IV include several iron-containing proteins known as cytochromes. The iron in these enzymes is located in substructures known as iron porphyrins (Figure 13.4.4). Like the Fe·S centers, the characteristic feature of the cytochromes is the ability of their iron atoms to exist as either Fe(II) or Fe(III). Thus, each cytochrome in its oxidized form—Fe(III)—can accept one electron and be reduced to the Fe(II) form. This change in oxidation state is reversible, so the reduced form can donate its electron to the next cytochrome, and so on. Complex III contains cytochromes b and c, as well as Fe·S proteins, with cytochrome c acting as the electron shuttle between complex III and IV. Complex IV contains cytochromes a and a_3 in an enzyme known as *cytochrome oxidase*. This enzyme has the ability to transfer electrons to molecular oxygen, the last electron acceptor in the chain of electron transport reactions. In this final step, water (H_2O) is formed.

- *Oxidation half-reaction*:

$$4\,\text{Cyt a}_3\text{-Fe(II)} \longrightarrow 4\,\text{Cyt a}_3\text{-Fe(III)} + 4\,e^-$$

- *Reduction half-reaction*:

$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$$

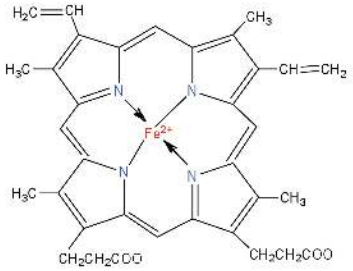


Figure 13.4.4: An Iron Porphyrin. Iron porphyrins are present in cytochromes as well as in myoglobin and hemoglobin.



Video: Cellular Respiration (Electron Transport Chain). Cellular respiration occurs in the mitochondria and provides both animals and plants with the energy needed to power other cellular processes. This section covers the electron transport chain.NDSU Virtual Cell Animations Project animation; ror more information please see Vcell, NDSU, Animations(opens in new window) [vcell.ndsu.edu]

Oxidative Phosphorylation

Each intermediate compound in the electron transport chain is reduced by the addition of one or two electrons in one reaction and then subsequently restored to its original form by delivering the electron(s) to the next compound along the chain. The successive electron transfers result in energy production. But how is this energy used for the synthesis of ATP? The process that links ATP synthesis to the operation of the electron transport chain is referred to as oxidative phosphorylation.

Electron transport is tightly coupled to oxidative phosphorylation. The coenzymes NADH and $FADH_2$ are oxidized by the respiratory chain *only* if ADP is simultaneously phosphorylated to ATP. The currently accepted model explaining how these two processes are linked is known as the *chemiosmotic hypothesis*, which was proposed by Peter Mitchell, resulting in Mitchell being awarded the 1978 Nobel Prize in Chemistry.

Looking again at Figure 13.4.3, we see that as electrons are being transferred through the electron transport chain, hydrogen (H^+) ions are being transported across the inner mitochondrial membrane from the matrix to the intermembrane space. The concentration of H^+ is already higher in the intermembrane space than in the matrix, so energy is required to transport the additional H^+ there. This energy comes from the electron transfer reactions in the electron transport chain. But how does the extreme difference in H^+ concentration then lead to ATP synthesis? The buildup of H^+ ions in the intermembrane space results in an H^+ ion gradient that is a large energy source, like water behind a dam (because, given the opportunity, the protons will flow out of the intermembrane space and into the less concentrated matrix). Current research indicates that the flow of H^+ down this concentration gradient through a

fifth enzyme complex, known as ATP synthase, leads to a change in the structure of the synthase, causing the synthesis and release of ATP.

In cells that are using energy, the turnover of ATP is very high, so these cells contain high levels of ADP. They must therefore consume large quantities of oxygen continuously, so as to have the energy necessary to phosphorylate ADP to form ATP. Consider, for example, that resting skeletal muscles use about 30% of a resting adult's oxygen consumption, but when the same muscles are working strenuously, they account for almost 90% of the total oxygen consumption of the organism.

Experiment has shown that 2.5–3 ATP molecules are formed for every molecule of NADH oxidized in the electron transport chain, and 1.5–2 ATP molecules are formed for every molecule of $FADH_2$ oxidized. Table 13.4.1 summarizes the theoretical maximum yield of ATP produced by the complete oxidation of 1 mol of acetyl-CoA through the sequential action of the citric acid cycle, the electron transport chain, and oxidative phosphorylation.

Table 13.4.1: Maximum Yield of ATP from the Complete Oxidation of 1 Mol of Acetyl-CoA

Reaction	Comments	Yield of ATP (moles)
Isocitrate → α-ketoglutarate + CO_2	produces 1 mol NADH	
α-ketoglutarate → succinyl-CoA + CO_2	produces 1 mol NADH	
Succinyl-CoA → succinate	produces 1 mol GTP	+1
Succinate → fumarate	produces 1 mol $FADH_2$	
Malate → oxaloacetate	produces 1 mol NADH	
1 $FADH_2$ from the citric acid cycle	yields 2 mol ATP	+2
3 NADH from the citric acid cycle	yields 3 mol ATP/NADH	+9
Net yield of ATP:		+12

Key Takeaways

- The acetyl group of acetyl-CoA enters the citric acid cycle. For each acetyl-CoA that enters the citric acid cycle, 2 molecules of carbon dioxide, 3 molecules of NADH, 1 molecule of ATP, and 1 molecule of $FADH_2$ are produced.
- The reduced coenzymes (NADH and $FADH_2$) produced by the citric acid cycle are reoxidized by the reactions of the electron transport chain. This series of reactions also produces a pH gradient across the inner mitochondrial membrane.
- The pH gradient produced by the electron transport chain drives the synthesis of ATP from ADP. For each NADH reoxidized, 2.5–3 molecules of ATP are produced; for each $FADH_2$ reoxidized, 1.5–2 molecules of ATP are produced.

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13.5: Stage II of Carbohydrate Catabolism

Learning Objectives

- Describe the function of glycolysis and identify its major products.
- Describe how the presence or absence of oxygen determines what happens to the pyruvate and the NADH that are produced in glycolysis.
- Determine the amount of ATP produced by the oxidation of glucose in the presence and absence of oxygen.

In stage II of catabolism, the metabolic pathway known as glycolysis converts glucose into two molecules of pyruvate (a three-carbon compound with three carbon atoms) with the corresponding production of adenosine triphosphate (ATP). The individual reactions in glycolysis were determined during the first part of the 20th century. It was the first metabolic pathway to be elucidated, in part because the participating enzymes are found in soluble form in the cell and are readily isolated and purified. The pathway is structured so that the product of one enzyme-catalyzed reaction becomes the substrate of the next. The transfer of intermediates from one enzyme to the next occurs by diffusion.

Steps in Glycolysis

The 10 reactions of glycolysis, summarized in Figures 13.5.1 and 13.5.2, can be divided into two phases. In the first 5 reactions—phase I—glucose is broken down into two molecules of glyceraldehyde 3-phosphate. In the last five reactions—phase II—each glyceraldehyde 3-phosphate is converted into pyruvate, and ATP is generated. Notice that all the intermediates in glycolysis are phosphorylated and contain either six or three carbon atoms.

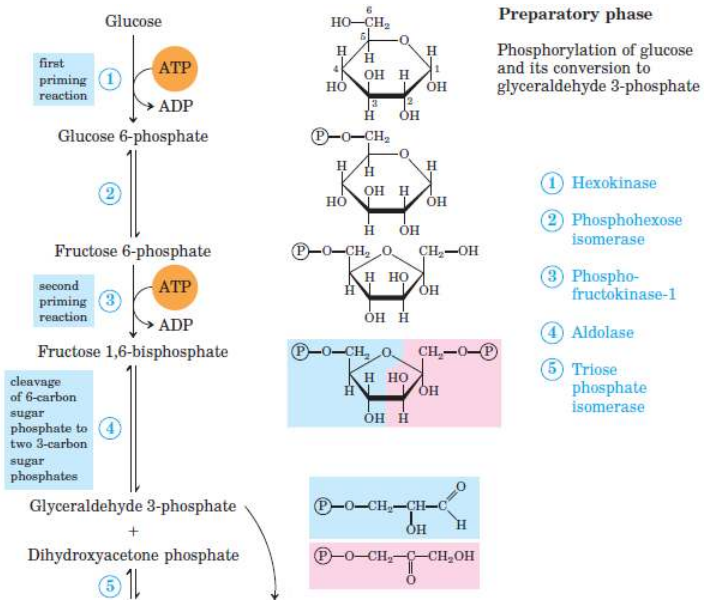


Figure 13.5.1: Phase 1 (preparatory phase) of Glycolysis

- When glucose enters a cell, it is immediately phosphorylated to form glucose 6-phosphate, in the first reaction of phase I. The phosphate donor in this reaction is ATP, and the enzyme—which requires magnesium ions for its activity—is *hexokinase*. In this reaction, ATP is being used rather than being synthesized. The presence of such a reaction in a catabolic pathway that is supposed to *generate* energy may surprise you. However, in addition to activating the glucose molecule, this initial reaction is essentially irreversible, an added benefit that keeps the overall process moving in the right direction. Furthermore, the addition of the negatively charged phosphate group prevents the intermediates formed in glycolysis from diffusing through the cell membrane, as neutral molecules such as glucose can do.
- In the next reaction, *phosphoglucose isomerase* catalyzes the isomerization of glucose 6-phosphate to fructose 6-phosphate. This reaction is important because it creates a primary alcohol, which can be readily phosphorylated.

- The subsequent phosphorylation of fructose 6-phosphate to form fructose 1,6-bisphosphate is catalyzed by *phosphofructokinase*, which requires magnesium ions for activity. ATP is again the phosphate donor.
- Fructose 1,6-bisphosphate is enzymatically cleaved by *aldolase* to form two triose phosphates: dihydroxyacetone phosphate and glyceraldehyde 3-phosphate.
- Isomerization of dihydroxyacetone phosphate into a second molecule of glyceraldehyde 3-phosphate is the final step in phase I. The enzyme catalyzing this reaction is *triose phosphate isomerase*.

When a molecule contains two phosphate groups on different carbon atoms, the convention is to use the prefix *bis*. When the two phosphate groups are bonded to each other on the same carbon atom (for example, adenosine diphosphate [ADP]), the prefix is *di*.

In steps 4 and 5, aldolase and triose phosphate isomerase effectively convert one molecule of fructose 1,6-bisphosphate into *two* molecules of glyceraldehyde 3-phosphate. Thus, phase I of glycolysis requires energy in the form of two molecules of ATP and releases none of the energy stored in glucose.

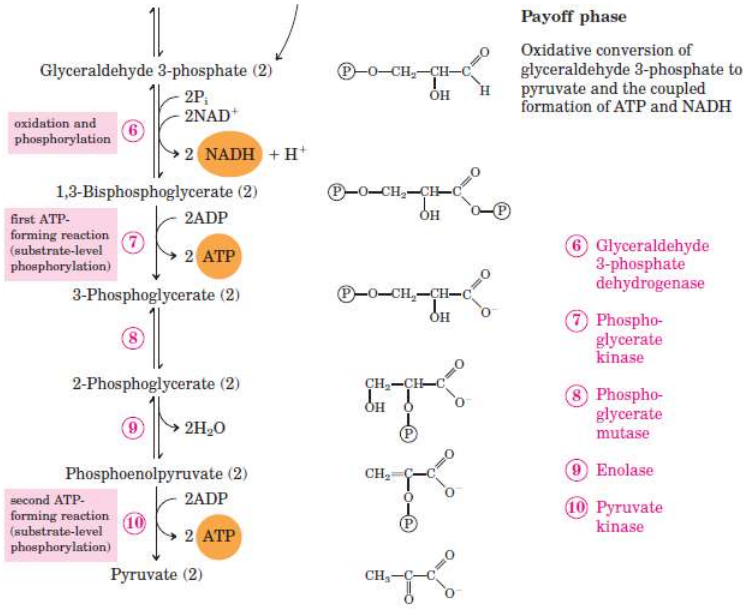


Figure 13.5.2: Phase 2 (payoff phase) of Glycolysis

In the initial step of phase II (Figure 13.5.2), glyceraldehyde 3-phosphate is both oxidized and phosphorylated in a reaction catalyzed by *glyceraldehyde-3-phosphate dehydrogenase*, an enzyme that requires nicotinamide adenine dinucleotide (NAD^+) as the oxidizing agent and inorganic phosphate as the phosphate donor. In the reaction, NAD^+ is reduced to reduced nicotinamide adenine dinucleotide (NADH), and 1,3-bisphosphoglycerate (BPG) is formed.

- BPG has a high-energy phosphate bond (Table 13.5.1) joining a phosphate group to C1. This phosphate group is now transferred directly to a molecule of ADP, thus forming ATP and 3-phosphoglycerate. The enzyme that catalyzes the reaction is **phosphoglycerate kinase**, which, like all other kinases, requires magnesium ions to function. This is the first reaction to produce ATP in the pathway. Because the ATP is formed by a direct transfer of a phosphate group from a metabolite to ADP—that is, from one substrate to another—the process is referred to as substrate-level phosphorylation, to distinguish it from the *oxidative phosphorylation* discussed in Section 20.4.
- In the next reaction, the phosphate group on 3-phosphoglycerate is transferred from the OH group of C3 to the OH group of C2, forming 2-phosphoglycerate in a reaction catalyzed by *phosphoglyceromutase*.
- A dehydration reaction, catalyzed by *enolase*, forms phosphoenolpyruvate (PEP), another compound possessing a high-energy phosphate group.

- The final step is irreversible and is the second reaction in which substrate-level phosphorylation occurs. The phosphate group of PEP is transferred to ADP, with one molecule of ATP being produced per molecule of PEP. The reaction is catalyzed by *pyruvate kinase*, which requires both magnesium and potassium ions to be active.

Table 13.5.1: Maximum Yield of ATP from the Complete Oxidation of 1 Mol of Glucose

Reaction	Comments	Yield of ATP (moles)
glucose → glucose 6-phosphate	consumes 1 mol ATP	−1
fructose 6-phosphate → fructose 1,6-bisphosphate	consumes 1 mol ATP	−1
glyceraldehyde 3-phosphate → BPG	produces 2 mol of cytoplasmic NADH	
BPG → 3-phosphoglycerate	produces 2 mol ATP	+2
phosphoenolpyruvate → pyruvate	produces 2 mol ATP	+2
pyruvate → acetyl-CoA + CO_2	produces 2 mol NADH	
isocitrate → α-ketoglutarate + CO_2	produces 2 mol NADH	
α-ketoglutarate → succinyl-CoA + CO_2	produces 2 mol NADH	
succinyl-CoA → succinate	produces 2 mol GTP	+2
succinate → fumarate	produces 2 mol $FADH_2$	
malate → oxaloacetate	produces 2 mol NADH	
2 cytoplasmic NADH from glycolysis	yields 2–3 mol ATP per NADH (depending on tissue)	+4 to +6
2 NADH from the oxidation of pyruvate	yields 3 mol ATP per NADH	+6
2 $FADH_2$ from the citric acid cycle	yields 2 ATP per $FADH_2$	+4
3 NADH from the citric acid cycle	yields 3 ATP per NADH	+18
Net yield of ATP:		+36 to +38

In phase II, two molecules of glyceraldehyde 3-phosphate are converted to two molecules of pyruvate, along with the production of four molecules of ATP and two molecules of NADH.

To Your Health: Diabetes

Although medical science has made significant progress against diabetes , it continues to be a major health threat. Some of the serious complications of diabetes are as follows:

- It is the leading cause of lower limb amputations in the United States.
- It is the leading cause of blindness in adults over age 20.
- It is the leading cause of kidney failure.
- It increases the risk of having a heart attack or stroke by two to four times.

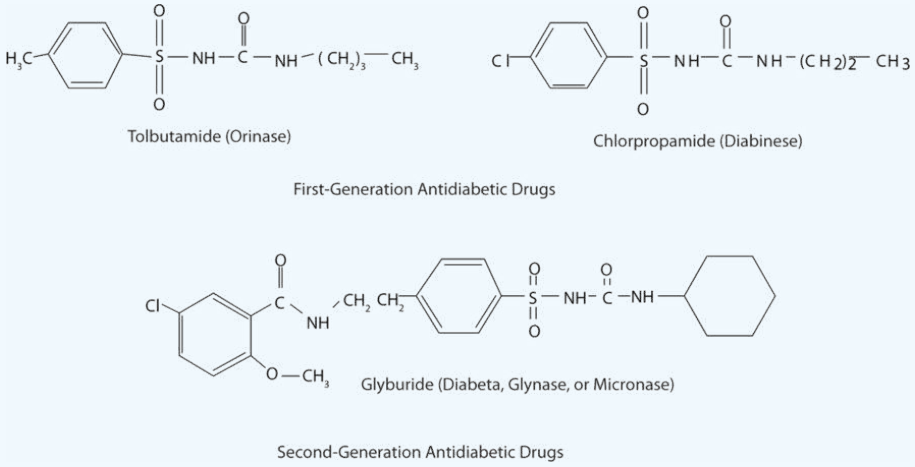
Because a person with diabetes is unable to use glucose properly, excessive quantities accumulate in the blood and the urine. Other characteristic symptoms are constant hunger, weight loss, extreme thirst, and frequent urination because the kidneys excrete large amounts of water in an attempt to remove excess sugar from the blood.

There are two types of diabetes. In immune-mediated diabetes, insufficient amounts of insulin are produced. This type of diabetes develops early in life and is also known as *Type 1 diabetes*, as well as insulin-dependent or juvenile-onset diabetes.

Symptoms are rapidly reversed by the administration of insulin, and Type 1 diabetics can lead active lives provided they receive insulin as needed. Because insulin is a protein that is readily digested in the small intestine, it cannot be taken orally and must be injected at least once a day.

In Type 1 diabetes, insulin-producing cells of the pancreas are destroyed by the body's immune system. Researchers are still trying to find out why. Meanwhile, they have developed a simple blood test capable of predicting who will develop Type 1 diabetes several years before the disease becomes apparent. The blood test reveals the presence of antibodies that destroy the body's insulin-producing cells.

Type 2 diabetes, also known as noninsulin-dependent or adult-onset diabetes, is by far the more common, representing about 95% of diagnosed diabetic cases. (This translates to about 16 million Americans.) Type 2 diabetics usually produce sufficient amounts of insulin, but either the insulin-producing cells in the pancreas do not release enough of it, or it is not used properly because of defective insulin receptors or a lack of insulin receptors on the target cells. In many of these people, the disease can be controlled with a combination of diet and exercise alone. For some people who are overweight, losing weight is sufficient to bring their blood sugar level into the normal range, after which medication is not required if they exercise regularly and eat wisely.



Those who require medication may use oral antidiabetic drugs that stimulate the islet cells to secrete insulin. First-generation antidiabetic drugs stimulated the release of insulin. Newer second-generation drugs, such as glyburide, do as well, but they also increase the sensitivity of cell receptors to insulin. Some individuals with Type 2 diabetes do not produce enough insulin and thus do not respond to these oral medications; they must use insulin. In both Type 1 and Type 2 diabetes, the blood sugar level must be carefully monitored and adjustments made in diet or medication to keep the level as normal as possible (70–120 mg/dL).

Metabolism of Pyruvate

The presence or absence of oxygen determines the fates of the pyruvate and the NADH produced in glycolysis. When plenty of oxygen is available, pyruvate is completely oxidized to carbon dioxide, with the release of much greater amounts of ATP through the combined actions of the citric acid cycle, the electron transport chain, and oxidative phosphorylation. However, in the absence of oxygen (that is, under anaerobic conditions), the fate of pyruvate is different in different organisms. In vertebrates, pyruvate is converted to lactate, while other organisms, such as yeast, convert pyruvate to ethanol and carbon dioxide. These possible fates of pyruvate are summarized in Figure 13.5.2. The conversion to lactate or ethanol under anaerobic conditions allows for the reoxidation of NADH to NAD^+ in the absence of oxygen.

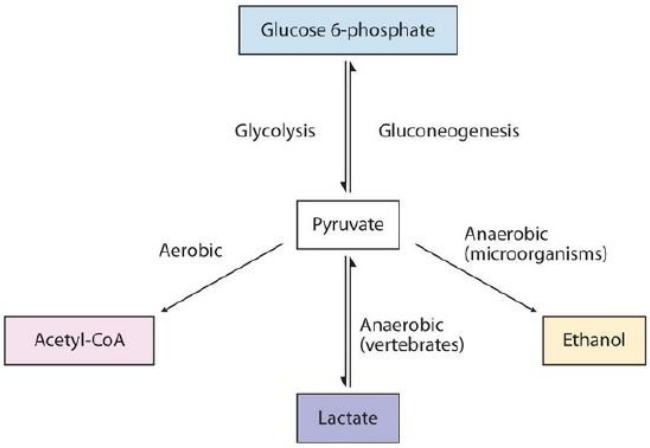


Figure 13.5.2: Metabolic Fates of Pyruvate

ATP Yield from Glycolysis

The net energy yield from anaerobic glucose metabolism can readily be calculated in moles of ATP. In the initial phosphorylation of glucose (step 1), 1 mol of ATP is expended, along with another in the phosphorylation of fructose 6-phosphate (step 3). In step 7, 2 mol of BPG (recall that 2 mol of 1,3-BPG are formed for each mole of glucose) are converted to 2 mol of 3-phosphoglycerate, and 2 mol of ATP are produced. In step 10, 2 mol of pyruvate and 2 mol of ATP are formed per mole of glucose.

For every mole of glucose degraded, 2 mol of ATP are initially consumed and 4 mol of ATP are ultimately produced. The net production of ATP is thus 2 mol for each mole of glucose converted to lactate or ethanol. If 7.4 kcal of energy is conserved per mole of ATP produced, and the total amount of energy that can theoretically be obtained from the complete oxidation of 1 mol of glucose is 670 kcal (as stated in the chapter introduction), the energy conserved in the anaerobic catabolism of glucose to two molecules of lactate (or ethanol) is as follows:

$$\frac{2 \times 7.4 \text{ kcal}}{670 \text{ kcal}} \times 100 = 2.2\%$$

Thus anaerobic cells extract only a very small fraction of the total energy of the glucose molecule.

Contrast this result with the amount of energy obtained when glucose is completely oxidized to carbon dioxide and water through glycolysis, the citric acid cycle, the electron transport chain, and oxidative phosphorylation as summarized in Table 13.5.1. Note the indication in the table that a variable amount of ATP is synthesized, depending on the tissue, from the NADH formed in the cytoplasm during glycolysis. This is because NADH is not transported into the inner mitochondrial membrane where the enzymes for the electron transport chain are located. Instead, brain and muscle cells use a transport mechanism that passes electrons from the cytoplasmic NADH through the membrane to flavin adenine dinucleotide (FAD) molecules inside the mitochondria, forming reduced flavin adenine dinucleotide ($FADH_2$), which then feeds the electrons into the electron transport chain. This route lowers the yield of ATP to 1.5–2 molecules of ATP, rather than the usual 2.5–3 molecules. A more efficient transport system is found in liver, heart, and kidney cells where the formation of one cytoplasmic NADH molecule results in the formation of one mitochondrial NADH molecule, which leads to the formation of 2.5–3 molecules of ATP.The total amount of energy conserved in the aerobic catabolism of glucose in the liver is as follows:

$$\frac{38 \times 7.4 \text{ kcal}}{670 \text{ kcal}} \times 100 = 42\%$$

Conservation of 42% of the total energy released compares favorably with the efficiency of any machine. In comparison, automobiles are only about 20%–25% efficient in using the energy released by the combustion of gasoline.

As indicated earlier, the 58% of released energy that is not conserved enters the surroundings (that is, the cell) as heat that helps to maintain body temperature. If we are exercising strenuously and our metabolism speeds up to provide the energy needed for muscle contraction, more heat is produced. We begin to perspire to dissipate some of that heat. As the perspiration evaporates, the excess heat is carried away from the body by the departing water vapor.

Summary

- The monosaccharide glucose is broken down through a series of enzyme-catalyzed reactions known as glycolysis.
- For each molecule of glucose that is broken down, two molecules of pyruvate, two molecules of ATP, and two molecules of NADH are produced.
- In the absence of oxygen, pyruvate is converted to lactate, and NADH is reoxidized to NAD+. In the presence of oxygen, pyruvate is converted to acetyl-CoA and then enters the citric acid cycle.
- More ATP can be formed from the breakdown of glucose when oxygen is present.

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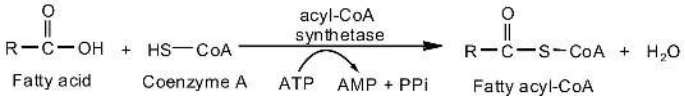
13.6: Stage II of Lipid Catabolism

Learning Objectives

- To describe the reactions needed to completely oxidize a fatty acid to carbon dioxide and water.

Like glucose, the fatty acids released in the digestion of triglycerides and other lipids are broken down in a series of sequential reactions accompanied by the gradual release of usable energy. Some of these reactions are oxidative and require nicotinamide adenine dinucleotide (NAD^+) and flavin adenine dinucleotide (FAD). The enzymes that participate in fatty acid catabolism are located in the mitochondria, along with the enzymes of the citric acid cycle, the electron transport chain, and oxidative phosphorylation. This localization of enzymes in the mitochondria is of the utmost importance because it facilitates efficient utilization of energy stored in fatty acids and other molecules.

Fatty acid oxidation is initiated on the outer mitochondrial membrane. There the fatty acids, which like carbohydrates are relatively inert, must first be activated by conversion to an energy-rich fatty acid derivative of coenzyme A called *fatty acyl-coenzyme A* (CoA). The activation is catalyzed by *acyl-CoA synthetase*. For each molecule of fatty acid activated, one molecule of coenzyme A and one molecule of adenosine triphosphate (ATP) are used, equaling a net utilization of the two high-energy bonds in one ATP molecule (which is therefore converted to adenosine monophosphate [AMP] rather than adenosine diphosphate [ADP]):



The fatty acyl-CoA diffuses to the inner mitochondrial membrane, where it combines with a carrier molecule known as carnitine in a reaction catalyzed by *carnitine acyltransferase*. The acyl-carnitine derivative is transported into the mitochondrial matrix and converted back to the fatty acyl-CoA.

Steps in the β-Oxidation of Fatty Acids

Further oxidation of the fatty acyl-CoA occurs in the mitochondrial matrix via a sequence of four reactions known collectively as β-oxidation because the β-carbon undergoes successive oxidations in the progressive removal of two carbon atoms from the carboxyl end of the fatty acyl-CoA (Figure 13.6.1).

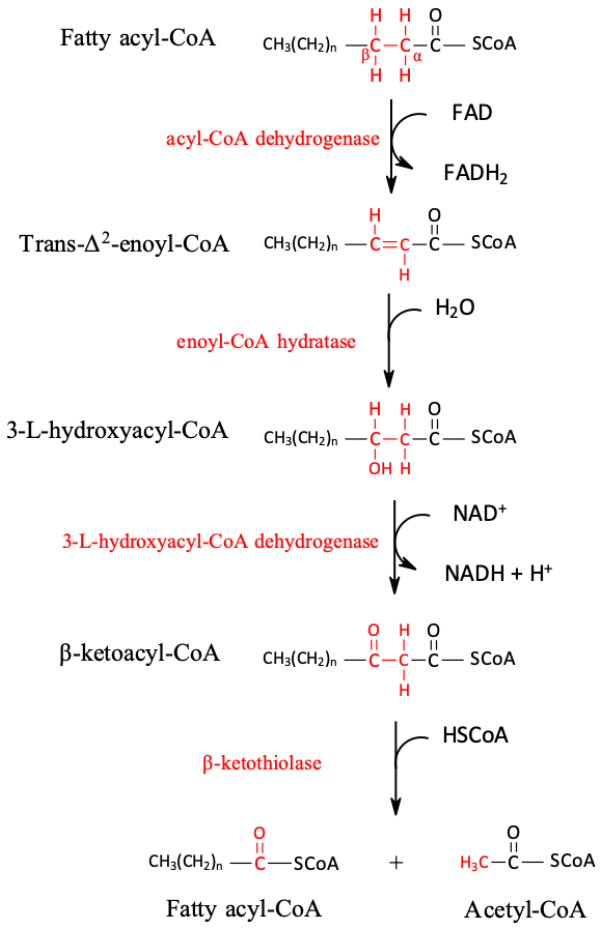


Figure 13.6.1: Fatty Acid Oxidation. The fatty acyl-CoA formed in the final step becomes the substrate for the first step in the next round of β-oxidation. β-oxidation continues until two acetyl-CoA molecules are produced in the final step.

The first step in the catabolism of fatty acids is the formation of an alkene in an oxidation reaction catalyzed by *acyl-CoA dehydrogenase*. In this reaction, the coenzyme FAD accepts two hydrogen atoms from the acyl-CoA, one from the α-carbon and one from the β-carbon, forming reduced flavin adenine dinucleotide ($FADH_2$).

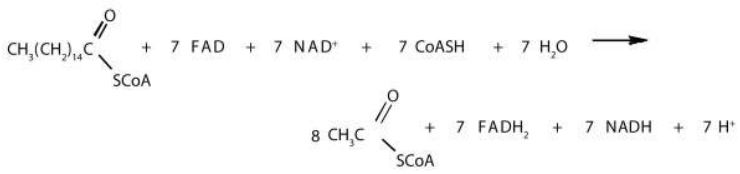
> The $FADH_2$ is reoxidized back to FAD via the electron transport chain that supplies energy to form 1.5–2 molecules of ATP.

Next, the *trans*-alkene is hydrated to form a secondary alcohol in a reaction catalyzed by *enoyl-CoA hydratase*. The enzyme forms only the L-isomer.

The secondary alcohol is then oxidized to a ketone by *β-hydroxyacyl-CoA dehydrogenase*, with NAD^+ acting as the oxidizing agent. The reoxidation of each molecule of NADH to NAD^+ by the electron transport chain furnishes 2.5–3 molecules of ATP.

The final reaction is cleavage of the β-ketoacyl-CoA by a molecule of coenzyme A. The products are acetyl-CoA and a fatty acyl-CoA that has been shortened by two carbon atoms. The reaction is catalyzed by *thiolase*.

The shortened fatty acyl-CoA is then degraded by repetitions of these four steps, each time releasing a molecule of acetyl-CoA. The overall equation for the β-oxidation of palmitoyl-CoA (16 carbon atoms) is as follows:

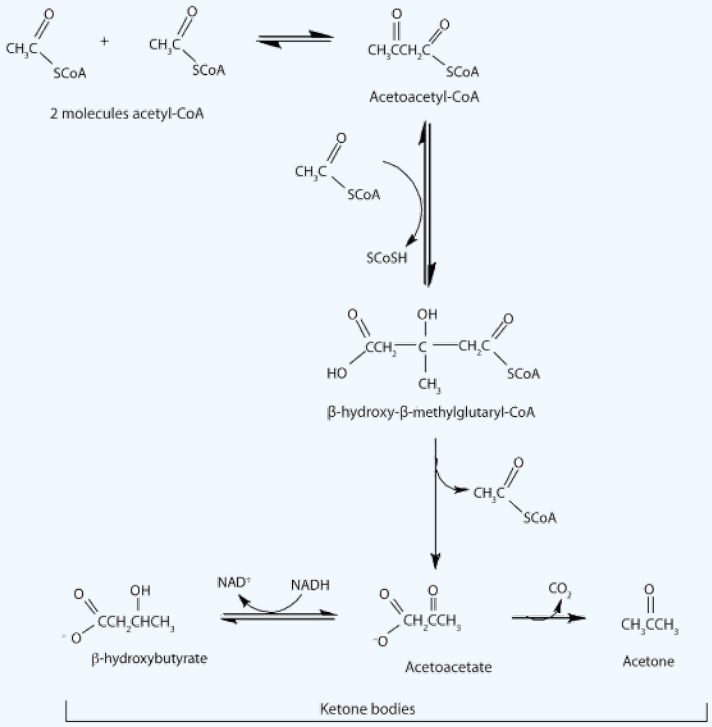


> *Because each shortened fatty acyl-CoA cycles back to the beginning of the pathway, β-oxidation is sometimes referred to as the fatty acid spiral.*

The fate of the acetyl-CoA obtained from fatty acid oxidation depends on the needs of an organism. It may enter the citric acid cycle and be oxidized to produce energy, it may be used for the formation of water-soluble derivatives known as ketone bodies, or it may serve as the starting material for the synthesis of fatty acids. For more information about the citric acid cycle, see Section 20.4.

Looking Closer: Ketone Bodies

In the liver, most of the acetyl-CoA obtained from fatty acid oxidation is oxidized by the citric acid cycle. However, some of the acetyl-CoA is used to synthesize a group of compounds known as *ketone bodies*: acetoacetate, β-hydroxybutyrate, and acetone. Two acetyl-CoA molecules combine, in a reversal of the final step of β-oxidation, to produce acetoacetyl-CoA. The acetoacetyl-CoA reacts with another molecule of acetyl-CoA and water to form β-hydroxy-β-methylglutaryl-CoA, which is then cleaved to acetoacetate and acetyl-CoA. Most of the acetoacetate is reduced to β-hydroxybutyrate, while a small amount is decarboxylated to carbon dioxide and acetone.



The acetoacetate and β-hydroxybutyrate synthesized by the liver are released into the blood for use as a metabolic fuel (to be converted back to acetyl-CoA) by other tissues, particularly the kidney and the heart. Thus, during prolonged starvation, ketone bodies provide about 70% of the energy requirements of the brain. Under normal conditions, the kidneys excrete about 20 mg of ketone bodies each day, and the blood levels are maintained at about 1 mg of ketone bodies per 100 mL of blood.

In starvation, diabetes mellitus, and certain other physiological conditions in which cells do not receive sufficient amounts of carbohydrate, the rate of fatty acid oxidation increases to provide energy. This leads to an increase in the concentration of acetyl-CoA. The increased acetyl-CoA cannot be oxidized by the citric acid cycle because of a decrease in the concentration of oxaloacetate, which is diverted to glucose synthesis. In response, the rate of ketone body formation in the liver increases further, to a level much higher than can be used by other tissues. The excess ketone bodies accumulate in the blood and the urine, a condition referred to as *ketosis*. When the acetone in the blood reaches the lungs, its volatility causes it to be expelled in the breath. The sweet smell of acetone, a characteristic of ketosis, is frequently noticed on the breath of severely diabetic patients.

Because two of the three kinds of ketone bodies are weak acids, their presence in the blood in excessive amounts overwhelms the blood buffers and causes a marked decrease in blood pH (to 6.9 from a normal value of 7.4). This decrease in pH leads to a serious condition known as *acidosis*. One of the effects of acidosis is a decrease in the ability of hemoglobin to transport oxygen in the blood. In moderate to severe acidosis, breathing becomes labored and very painful. The body also loses fluids and becomes dehydrated as the kidneys attempt to get rid of the acids by eliminating large quantities of water. The lowered oxygen supply and dehydration lead to depression; even mild acidosis leads to lethargy, loss of appetite, and a generally run-down feeling. Untreated patients may go into a coma. At that point, prompt treatment is necessary if the person's life is to be saved.

ATP Yield from Fatty Acid Oxidation

The amount of ATP obtained from fatty acid oxidation depends on the size of the fatty acid being oxidized. For our purposes here. we'll study palmitic acid, a saturated fatty acid with 16 carbon atoms, as a typical fatty acid in the human diet. Calculating its energy yield provides a model for determining the ATP yield of all other fatty acids.

The breakdown by an organism of 1 mol of palmitic acid requires 1 mol of ATP (for activation) and forms 8 mol of acetyl-CoA. Recall from Table 20.4.1 that each mole of acetyl-CoA metabolized by the citric acid cycle yields 10 mol of ATP. The complete degradation of 1 mol of palmitic acid requires the β-oxidation reactions to be repeated seven times. Thus, 7 mol of NADH and 7 mol of $FADH_2$ are produced. Reoxidation of these compounds through respiration yields 2.5–3 and 1.5–2 mol of ATP, respectively. The energy calculations can be summarized as follows:

ATP Yield from Fatty Acid Oxidation

1 mol of ATP is split to AMP and $2P_i$	−2 ATP
8 mol of acetyl-CoA formed (8 × 12)	96 ATP
7 mol of $FADH_2$ formed (7 × 2)	14 ATP
7 mol of NADH formed (7 × 3)	21 ATP
Total	129 ATP

> *The number of times β-oxidation is repeated for a fatty acid containing n carbon atoms is n/2 – 1 because the final turn yields two acetyl-CoA molecules.*

The combustion of 1 mol of palmitic acid releases a considerable amount of energy:

$$C_{16}H_{32}O_2 + 23O_2 \rightarrow 16CO_2 + 16H_2O + 2,340\ kcal$$

The percentage of this energy that is conserved by the cell in the form of ATP is as follows:

$$\frac{\text{energy conserved}}{\text{total energy available}} \times 100 = \frac{(129\ \text{ATP})(7.4\ \text{kcal/ATP})}{2,340\ \text{kcal}} \times 100 = 41\%$$

The efficiency of fatty acid metabolism is comparable to that of carbohydrate metabolism, which we calculated to be 42%. For more information about the efficiency of fatty acid metabolism, see II of Carbohydrate Catabolism" data-cke-saved-href="/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/20:_Energy_Metabolism/20.05:_Stage_II_of_Carbohydrate_Catabolism" href="/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/20:_Energy_Metabolism/20.05:_Stage_II_of_Carbohydrate_Catabolism" data-quail-id="91">Section 20.5.

> *The oxidation of fatty acids produces large quantities of water. This water, which sustains migratory birds and animals (such as the camel) for long periods of time.*

Summary

- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β-oxidation.
- In each round of β-oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

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13.7: Stage II of Protein Catabolism

Learning Objectives

- To describe how excess amino acids are degraded.

The liver is the principal site of amino acid metabolism, but other tissues, such as the kidney, the small intestine, muscles, and adipose tissue, take part. Generally, the first step in the breakdown of amino acids is the separation of the amino group from the carbon skeleton, usually by a transamination reaction. The carbon skeletons resulting from the deaminated amino acids are used to form either glucose or fats, or they are converted to a metabolic intermediate that can be oxidized by the citric acid cycle. The latter alternative, amino acid catabolism, is more likely to occur when glucose levels are low—for example, when a person is fasting or starving.

Transamination

Transamination is an exchange of functional groups between any amino acid (except lysine, proline, and threonine) and an α-keto acid. The amino group is usually transferred to the keto carbon atom of pyruvate, oxaloacetate, or α-ketoglutarate, converting the α-keto acid to alanine, aspartate, or glutamate, respectively. Transamination reactions are catalyzed by specific transaminases (also called aminotransferases), which require pyridoxal phosphate as a coenzyme.

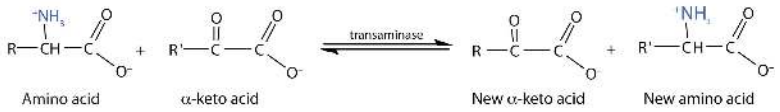


Figure 13.7.1).

> *In an α-keto acid, the carbonyl or keto group is located on the carbon atom adjacent to the carboxyl group of the acid.*

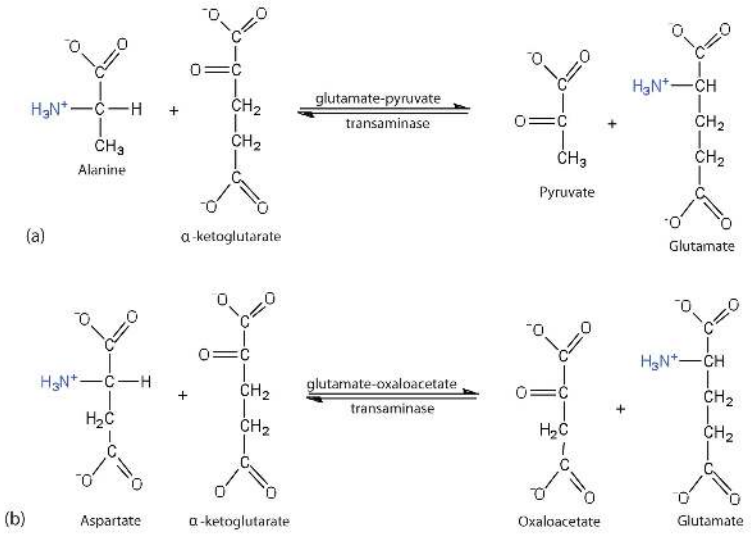
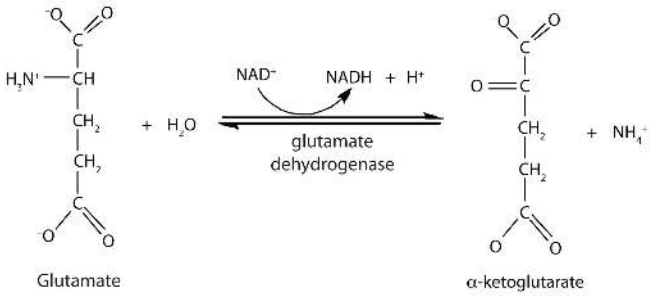


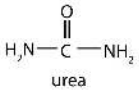
Figure 13.7.1: Two Transamination Reactions. In both reactions, the final acceptor of the amino group is α-ketoglutarate, and the final product is glutamate.

Oxidative Deamination

In the breakdown of amino acids for energy, the final acceptor of the α-amino group is α-ketoglutarate, forming glutamate. Glutamate can then undergooxidative deamination, in which it loses its amino group as an ammonium (NH_4^+) ion and is oxidized back to α-ketoglutarate (ready to accept another amino group):



This reaction occurs primarily in liver mitochondria. Most of the NH_4^+ ion formed by oxidative deamination of glutamate is converted to urea and excreted in the urine in a series of reactions known as the **urea cycle**.



The synthesis of glutamate occurs in animal cells by reversing the reaction catalyzed by glutamate dehydrogenase. For this reaction nicotinamide adenine dinucleotide phosphate (NADPH) acts as the reducing agent. The synthesis of glutamate is significant because it is one of the few reactions in animals that can incorporate inorganic nitrogen (NH_4^+) into an α-keto acid to form an amino acid. The amino group can then be passed on through transamination reactions, to produce other amino acids from the appropriate α-keto acids.

The Fate of the Carbon Skeleton

Any amino acid can be converted into an intermediate of the citric acid cycle. Once the amino group is removed, usually by transamination, the α-keto acid that remains is catabolized by a pathway unique to that acid and consisting of one or more reactions. For example, phenylalanine undergoes a series of six reactions before it splits into fumarate and acetoacetate. Fumarate is an intermediate in the citric acid cycle, while acetoacetate must be converted to acetoacetyl-coenzyme A (CoA) and then to acetyl-CoA before it enters the citric acid cycle.

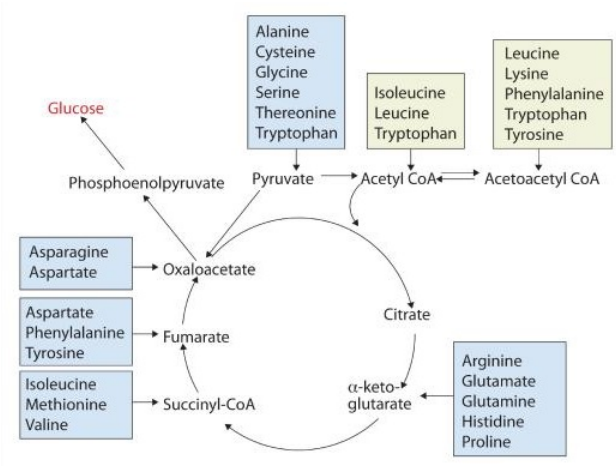


Figure 13.7.2: Fates of the Carbon Skeletons of Amino Acids

Those amino acids that can form any of the intermediates of carbohydrate metabolism can subsequently be converted to glucose via a metabolic pathway known as gluconeogenesis. These amino acids are called glucogenic amino acids. Amino acids that are converted to acetoacetyl-CoA or acetyl-CoA, which can be used for the synthesis of ketone bodies but not glucose, are called ketogenic amino acids. Some amino acids fall into both categories. Leucine and lysine are the only amino acids that are exclusively ketogenic. Figure 13.7.2 summarizes the ultimate fates of the carbon skeletons of the 20 amino acids.

Career Focus: Exercise Physiologist

An exercise physiologist works with individuals who have or wish to prevent developing a wide variety of chronic diseases, such as diabetes, in which exercise has been shown to be beneficial. Each individual must be referred by a licensed physician. An exercise physiologist works in a variety of settings, such as a hospital or in a wellness program at a commercial business, to design and monitor individual exercise plans. A registered clinical exercise physiologist must have an undergraduate degree in exercise physiology or a related degree. Some job opportunities require a master's degree in exercise physiology or a related degree.



Ergospirometry laboratory for the measurement of metabolic changes during a graded exercise test on a treadmill. from Wikipedia.

Summary

Generally the first step in the breakdown of amino acids is the removal of the amino group, usually through a reaction known as transamination. The carbon skeletons of the amino acids undergo further reactions to form compounds that can either be used for the synthesis of glucose or the synthesis of ketone bodies.

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13.E: Energy Metabolism (Exercises)

20.1: ATP- the Universal Energy Currency

Concept Review Exercise

1. Why is ATP referred to as the energy currency of the cell?

Answer

1. ATP is the principal molecule involved in energy exchange reactions in biological systems.

Exercises

1. How do ATP and ADP differ in structure?
2. Why does the hydrolysis of ATP to ADP involve the release of energy?
3. Identify whether each compound would be classified as a high-energy phosphate compound.
   a. ATP
   b. glucose 6-phosphate
   c. creatine phosphate
4. Identify whether each compound would be classified as a high-energy phosphate compound.
   a. ADP
   b. AMP
   c. glucose 1-phosphate

Answers

1. ATP has a triphosphate group attached, while ADP has only a diphosphate group attached.

3. a. yes
   b. no
   c. yes

20.2: Stage I of Catabolism

Concept Review Exercises

1. Distinguish between each pair of compounds.
   a. pepsin and pepsinogen
   b. chymotrypsin and trypsin
   c. aminopeptidase and carboxypeptidase
2. What are the primary end products of each form of digestion?
   a. carbohydrate digestion
   b. lipid digestion
   c. protein digestion
3. In what section of the digestive tract does most of the carbohydrate, lipid, and protein digestion take place?

Answers

1. a. Pepsinogen is an inactive form of pepsin; pepsin is the active form of the enzyme.
   b. Both enzymes catalyze the hydrolysis of peptide bonds. Chymotrypsin catalyzes the hydrolysis of peptide bonds following aromatic amino acids, while trypsin catalyzes the hydrolysis of peptide bonds following lysine and arginine.
   c. Aminopeptidase catalyzes the hydrolysis of amino acids from the N-terminal end of a protein, while carboxypeptidase catalyzes the hydrolysis of amino acids from the C-terminal end of a protein.
2. a. glucose, fructose, and galactose

b. monoglycerides and fatty acids
c. amino acids

3. the small intestine

Exercises

1. What are the products of digestion (or stage I of catabolism)?
2. What is the general type of reaction used in digestion?
3. Give the site of action and the function of each enzyme.
   a. chymotrypsin
   b. lactase
   c. pepsin
   d. maltase
4. Give the site of action and the function of each enzyme.
   a. α-amylase
   b. trypsin
   c. sucrase
   d. aminopeptidase
5. a. What is the meaning of the following statement? “Bile salts act to emulsify lipids in the small intestine.”
   b. Why is emulsification important?
6. Using chemical equations, describe the chemical changes that triglycerides undergo during digestion.
7. What are the expected products from the enzymatic action of chymotrypsin on each amino acid segment?
   a. gly-ala-phe-thr-leu
   b. ala-ile-tyr-ser-arg
   c. val-trp-arg-leu-cys
8. What are the expected products from the enzymatic action of trypsin on each amino acid segment?
   a. leu-thr-glu-lys-ala
   b. phe-arg-ala-leu-val
   c. ala-arg-glu-trp-lys

Answers

1. proteins: amino acids; carbohydrates: monosaccharides; fats: fatty acids and glycerol
3. a. Chymotrypsin is found in the small intestine and catalyzes the hydrolysis of peptide bonds following aromatic amino acids.
   b. Lactase is found in the small intestine and catalyzes the hydrolysis of lactose.
   c. Pepsin is found in the stomach and catalyzes the hydrolysis of peptide bonds, primarily those that occur after aromatic amino acids.
   d. Maltase is found in the small intestine and catalyzes the hydrolysis of maltose.
5. a. Bile salts aid in digestion by dispersing lipids throughout the aqueous solution in the small intestine.
   b. Emulsification is important because lipids are not soluble in water; it breaks lipids up into smaller particles that can be more readily hydrolyzed by lipases.
7. a. gly-ala-phe and thr-leu
   b. ala-ile-tyr and ser-arg
   c. val-trp and arg-leu-cys

20.3: Overview of Stage II of Catabolism

Concept Review Exercises

1. What is a metabolic pathway?
2. What vitamin is required to make coenzyme A?
3. What is the net yield of Glycolysis as far as ATP?
4. Name the enzymes that are key regulatory sites in Glycolysis.
5. Why are the enzymes in the previous question targets for regulation?
6. Why is the priming phase necessary?
7. Draw the entire pathway for glycolysis including enzymes, reactants and products for each step.
8. Where does beta-oxidation occur?
9. What is the average net yield of ATP per carbon?
10. Where exactly is water formed during the process of fatty acid degradation? (Hint: H_2O is formed when when the one of the products of beta-oxidation is passed through another of the metabolic pathways)
11. During the process of beta-oxidation, why is it that [FAD] is used to oxidize an alkane to an alkene while NAD^+ is used to oxidize an alchol to a carbonyl
12. Draw out the entire process of the degradation of a triglyceride, include enzymes and products and reactants for each step.

Answers

1. A metabolic pathway is a series of biochemical reactions by which an organism converts a given reactant to a specific end product.
2. pantothenic acid

20.4: Stage III of Catabolism

Concept Review Exercises

1. What is the main function of the citric acid cycle?
2. Two carbon atoms are fed into the citric acid cycle as acetyl-CoA. In what form are two carbon atoms removed from the cycle?
3. What are mitochondria and what is their function in the cell?

Answers

1. the complete oxidation of carbon atoms to carbon dioxide and the formation of a high-energy phosphate compound, energy rich reduced coenzymes (NADH and $FADH_2$), and metabolic intermediates for the synthesis of other compounds
2. as carbon dioxide
3. Mitochondria are small organelles with a double membrane that contain the enzymes and other molecules needed for the production of most of the ATP needed by the body.

Exercises

1. Replace each question mark with the correct compound.
   a. $? \xrightarrow{\text{aconitase}} \text{isocitrate}$
   b. $? + ? \xrightarrow{\text{citrate synthase}} \text{citrate} + \text{coenzyme A}$
   c. $\text{fumarate} \xrightarrow{\text{fumarase}} ?$
   d. $\text{isocitrate} + NAD^+ \xrightarrow{?} \alpha\text{-ketoglurate} + NADH + CO_2$

2. Replace each question mark with the correct compound.

   a. $\text{malate} + \text{NAD}^+ \xrightarrow{?} \text{oxaloacetate} + \text{NADH}$

   b. $? + ? \xrightarrow{\text{nucleoside diphosphokinase}} \text{GDP} + \text{ATP}$

   c. $\text{succinyl-CoA} \xrightarrow{\text{succinyl-CoA synthetase}} ? + ?$

   d. $\text{succinate} + \text{FAD} \xrightarrow{\text{succinate dehydrogenase}} ? + \text{FADH}_2$

3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

   a. isomerization

   b. hydration

   c. synthesis

4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

   a. oxidation

   b. decarboxylation

   c. phosphorylation

5. What similar role do coenzyme Q and cytochrome c serve in the electron transport chain?

6. What is the electron acceptor at the end of the electron transport chain? To what product is this compound reduced?

7. What is the function of the cytochromes in the electron transport chain?

8. a. What is meant by this statement? “Electron transport is tightly coupled to oxidative phosphorylation.”

   b. How are electron transport and oxidative phosphorylation coupled or linked?

Answers

1. a. citrate

   b. oxaloacetate + acetyl-CoA

   c. malate

   d. α-ketoglutarate hydrogenase complex

3. a. reaction in 1a

   b. reaction in 1c

   c. reaction in 1b

5. Both molecules serve as electron shuttles between the complexes of the electron transport chain.

7. Cytochromes are proteins in the electron transport chain and serve as one-electron carriers.

20.5: Stage II of Carbohydrate Catabolism

- ### Concept Review Exercises

  1. In glycolysis, how many molecules of pyruvate are produced from one molecule of glucose?

  2. In vertebrates, what happens to pyruvate when

     a. plenty of oxygen is available?

     b. oxygen supplies are limited?

  3. In anaerobic glycolysis, how many molecules of ATP are produced from one molecule of glucose?

  #### Answers

  1. two

  2. a. Pyruvate is completely oxidized to carbon dioxide.

     b. Pyruvate is reduced to lactate, allowing for the reoxidation of NADH to NAD^+.

  3. There is a net production of two molecules of ATP.

Exercises

1. Replace each question mark with the correct compound.
   a. $\text{fructose 1,6-bisphosphate} \xrightarrow{\text{aldolase}} ? + ?$
   b. $? + \text{ADP} \xrightarrow{\text{pyruvate kinase}} \text{pyruvate} + \text{ATP}$
   c. $\text{dihydroxyacetone phosphate} \xrightarrow{?} \text{glyceraldehyde 3-phosphate}$
   d. $\text{glucose} + \text{ATP} \xrightarrow{\text{hexokinase}} ? + \text{ADP}$
2. Replace each question mark with the correct compound.
   a. $\text{fructose 6-phosphate} + \text{ATP} \xrightarrow{?} \text{fructose 1,6-bisphosphate} + \text{ADP}$
   b. $? \xrightarrow{\text{phosphoglucose isomerase}} \text{fructose 6-phosphate}$
   c. $\text{glyceraldehyde 3-phosphate} + \text{NAD}^+ + \text{P}_\text{i} \xrightarrow{?} \text{1,3-bisphosphoglycerate} + \text{NADH}$
   d. $\text{3-phosphoglycerate} \xrightarrow{\text{phosphoglyceromutase}} ?$
3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
   a. hydrolysis of a high-energy phosphate compound
   b. synthesis of ATP
4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
   a. isomerization
   b. oxidation
5. What coenzyme is needed as an oxidizing agent in glycolysis?
6. Calculate
   a. the *total* number of molecules of ATP produced for each molecule of glucose converted to pyruvate in glycolysis.
   b. the number of molecules of ATP hydrolyzed in phase I of glycolysis.
   c. the *net* ATP production from glycolysis alone.
7. How is the NADH produced in glycolysis reoxidized when oxygen supplies are limited in
   a. muscle cells?
   b. yeast?
8. a. Calculate the number of moles of ATP produced by the aerobic oxidation of 1 mol of glucose in a liver cell.
   b. Of the total calculated in Exercise 9a, determine the number of moles of ATP produced in each process.
      a. glycolysis alone
      b. the citric acid cycle
      c. the electron transport chain and oxidative phosphorylation

Answers

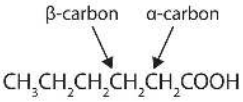
1. a. glyceraldehyde 3-phosphate + dihydroxyacetone phosphate
   b. phosphoenolpyruvate
   c. triose phosphate isomerase
   d. glucose 6-phosphate
3. a. reactions 1b, 1d, and 2a
   b. reaction 1b
5. NAD^+
7. a. Pyruvate is reduced to lactate, and NADH is reoxidized to NAD^+.
   b. Pyruvate is converted to ethanol and carbon dioxide, and NADH is reoxidized to NAD^+.

20.6: Stage II of Lipid Catabolism

- ### Concept Review Exercises

1. How are fatty acids activated prior to being transported into the mitochondria and oxidized?
2. Draw the structure of hexanoic (caproic) acid and identify the α-carbon and the β-carbon.

Answers

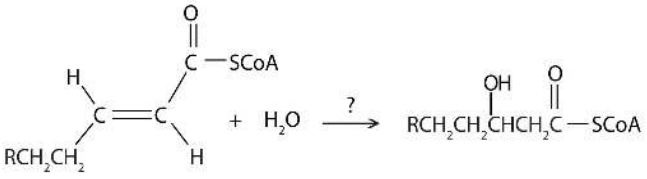
1. They react with CoA to form fatty acyl-CoA molecules.
2. 

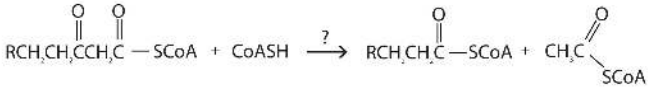
Key Takeaways

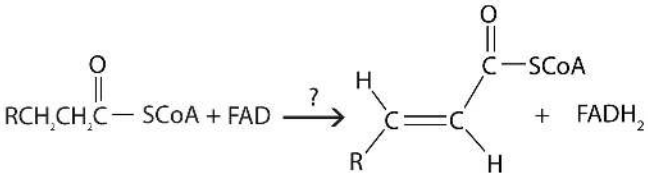
- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β-oxidation.
- In each round of β-oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

Exercises

1. For each reaction found in β-oxidation, identify the enzyme that catalyzes the reaction and classify the reaction as oxidation-reduction, hydration, or cleavage.

a. 

b. 

c. 

2. What are the products of β-oxidation?
3. How many rounds of β-oxidation are necessary to metabolize lauric acid (a saturated fatty acid with 12 carbon atoms)?
4. How many rounds of β-oxidation are necessary to metabolize arachidic acid (a saturated fatty acid with 20 carbon atoms)?
5. When myristic acid (a saturated fatty acid with 14 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA
   b. $FADH_2$
   c. NADH
6. When stearic acid (a saturated fatty acid with 18 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA

b. $FADH_2$

c. NADH

7. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of myristic acid?
8. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of stearic acid?

Answers

1. a. enoyl-CoA hydratase; hydration

   b. thiolase; cleavage

   c. acyl-CoA dehydrogenase; oxidation-reduction

3. five rounds
5. a. 7 molecules

   b. 6 molecules

   c. 6 molecules

7. 112 molecules

20.7: Stage II of Protein Catabolism

Concept Review Exercises

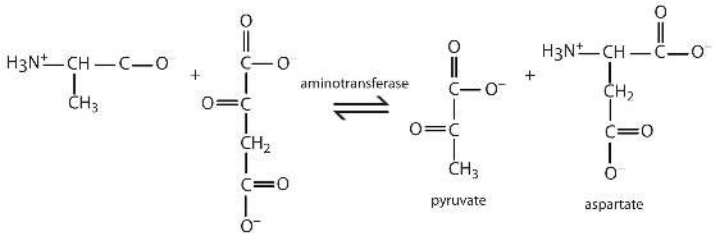
1. a. Write the equation for the transamination reaction between alanine and oxaloacetate.

   b. Name the two products that are formed.

2. What is the purpose of oxidative deamination?

Answers

1. a.



   b. pyruvate and aspartate

2. Oxidative deamination provides a reaction in which the amino group [as the ammonium (NH_4^+) ion] is removed from a molecule, not simply transferred from one molecule to another. Most of the NH_4^+ ion is converted to urea and excreted from the body.

Exercises

1. Write the equation for the transamination reaction between valine and pyruvate.
2. Write the equation for the transamination reaction between phenylalanine and oxaloacetate.
3. What products are formed in the oxidative deamination of glutamate?
4. Determine if each amino acid is glucogenic, ketogenic, or both.

   a. phenylalanine

   b. leucine

   c. serine

5. Determine if each amino acid is glucogenic, ketogenic, or both.

   a. asparagine

   b. tyrosine

   c. valine

Answers



1.

3. α-ketoglutarate, NADH, and NH_4^+

5. a. glucogenic
   b. both
   c. glucogenic

Additional Exercises

1. Hydrolysis of which compound—arginine phosphate or glucose 6-phosphate—would provide enough energy for the phosphorylation of ATP? Why?
2. If a cracker, which is rich in starch, is chewed for a long time, it begins to develop a sweet, sugary taste. Why?
3. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.

   a. aminopeptidase
   b. chymotrypsin

4. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.

   a. trypsin
   b. carboxypeptidase

5. If the methyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?
6. If the carbonyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?
7. The average adult consumes about 65 g of fructose daily (either as the free sugar or from the breakdown of sucrose). In the liver, fructose is first phosphorylated to fructose 1-phosphate, which is then split into dihydroxyacetone phosphate and glyceraldehyde. Glyceraldehyde is then phosphorylated to glyceraldehyde 3-phosphate, with ATP as the phosphate group donor. Write the equations (using structural formulas) for these three steps. Indicate the type of enzyme that catalyzes each step.
8. What critical role is played by both BPG and PEP in glycolysis?
9. How is the NADH produced in glycolysis reoxidized when oxygen supplies are abundant?
10. When a triglyceride is hydrolyzed to form three fatty acids and glycerol, the glycerol can be converted to glycerol 3-phosphate and then oxidized to form dihydroxyacetone phosphate, an intermediate of glycolysis. (In this reaction, NAD^+ is reduced to NADH.) If you assume that there is sufficient oxygen to completely oxidize the pyruvate formed from dihydroxyacetone phosphate, what is the maximum amount of ATP formed from the complete oxidation of 1 mol of glycerol?
11. How is the $FADH_2$ from β-oxidation converted back to FAD?
12. If 1 mol of alanine is converted to pyruvate in a muscle cell (through transamination) and the pyruvate is then metabolized via the citric acid cycle, the electron transport chain, and oxidative phosphorylation, how many moles of ATP are produced?
13. If the essential amino acid leucine (2-amino-4-methylpentanoic acid) is lacking in the diet, an α-keto acid can substitute for it. Give the structure of the α-keto acid and the probable reaction used to form leucine from this α-keto acid.

Answers

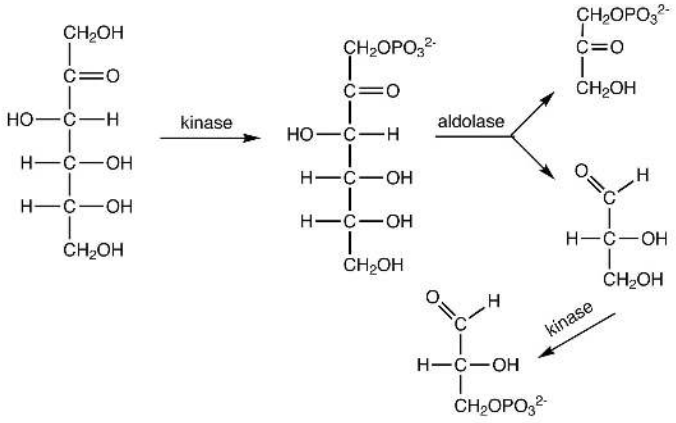
1. The hydrolysis of arginine phosphate releases more energy than is needed for the synthesis of ATP, while hydrolysis of glucose 6-phosphate does not.

3.

a. The enzyme will cleave off amino acids one at a time beginning with alanine (the N-terminal end).
b. following phenylalanine

5. Half of the label will be on the second carbon atom of oxaloacetate, while the other half will be on the third carbon atom.

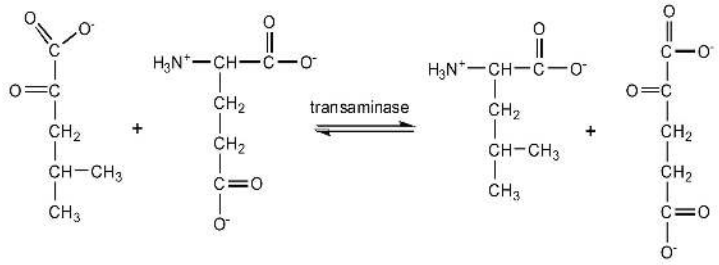
7.



9. When oxygen is abundant, NADH is reoxidized through the reactions of the electron transport chain.

11. $FADH_2$ is reoxidized back to FAD via the electron transport chain.

13.



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13.S: Energy Metabolism (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.

Metabolism is the general term for all chemical reactions in living organisms. The two types of metabolism are **catabolism**—those reactions in which complex molecules (carbohydrates, lipids, and proteins) are broken down to simpler ones with the concomitant release of energy—and **anabolism**—those reactions that consume energy to build complex molecules. Metabolism is studied by looking at individual **metabolic pathways**, which are a series of biochemical reactions in which a given reactant is converted to a desired end product.

The oxidation of fuel molecules (primarily carbohydrates and lipids), a process called **respiration**, is the source of energy used by cells. Catabolic reactions release energy from food molecules and use some of that energy for the synthesis of *adenosine triphosphate* (ATP); anabolic reactions use the energy in ATP to create new compounds. Catabolism can be divided into three stages. In stage I, carbohydrates, lipids, and proteins are broken down into their individual monomer units—simple sugars, fatty acids, and amino acids, respectively. In stage II, these monomer units are broken down by specific metabolic pathways to form a common end product *acetyl-coenzyme A* (CoA). In stage III, acetyl-CoA is completely oxidized to form carbon dioxide and water, and ATP is produced.

The **digestion** of carbohydrates begins in the mouth as α-amylase breaks glycosidic linkages in carbohydrate molecules. Essentially no carbohydrate digestion occurs in the stomach, and food particles pass through to the small intestine, where α-amylase and intestinal enzymes convert complex carbohydrate molecules (starches) to monosaccharides. The monosaccharides then pass through the lining of the small intestine and into the bloodstream for transport to all body cells.

Protein digestion begins in the stomach as pepsinogen in **gastric juice** is converted to pepsin, the enzyme that hydrolyzes peptide bonds. The partially digested protein then passes to the small intestine, where the remainder of protein digestion takes place through the action of several enzymes. The resulting amino acids cross the intestinal wall into the blood and are carried to the liver.

Lipid digestion begins in the small intestine. Bile salts emulsify the lipid molecules, and then lipases hydrolyze them to fatty acids and monoglycerides. The hydrolysis products pass through the intestine and are repackaged for transport in the bloodstream.

In cells that are operating aerobically, acetyl-CoA produced in stage II of catabolism is oxidized to carbon dioxide. The **citric acid cycle** describes this oxidation, which takes place with the formation of the coenzymes reduced nicotinamide adenine dinucleotide (NADH) and reduced flavin adenine dinucleotide ($FADH_2$). The sequence of reactions needed to oxidize these coenzymes and transfer the resulting electrons to oxygen is called the **electron transport chain**, or the **respiratory chain**. The compounds responsible for this series of oxidation-reduction reactions include proteins known as **cytochromes**, Fe·S proteins, and other molecules that ultimately result in the reduction of molecular oxygen to water. Every time a compound with two carbon atoms is oxidized in the citric acid cycle, a respiratory chain compound accepts the electrons lost in the oxidation (and so is reduced) and then passes them on to the next metabolite in the chain. The energy released by the electron transport chain is used to transport hydrogen (H^+) ions from the mitochondrial matrix to the intermembrane space. The flow of H^+ back through ATP synthase leads to the synthesis and release of ATP from adenosine diphosphate (ADP) and inorganic phosphate ions (P_i) in a process known as **oxidative phosphorylation**. Electron transport and oxidative phosphorylation are tightly coupled to each other. The enzymes and intermediates of the citric acid cycle, the electron transport chain, and oxidative phosphorylation are located in organelles called **mitochondria**.

The oxidation of carbohydrates is the source of over 50% of the energy used by cells. Glucose is oxidized to two molecules of pyruvate through a series of reactions known as **glycolysis**. Some of the energy released in these reactions is conserved by the formation of ATP from ADP. Glycolysis can be divided into two phases: phase I consists of the first five reactions and requires energy to “prime” the glucose molecule for phase II, the last five reactions in which ATP is produced through **substrate-level phosphorylation**.

The pyruvate produced by glycolysis has several possible fates, depending on the organism and whether or not oxygen is present. In animal cells, pyruvate can be further oxidized to acetyl-CoA and then to carbon dioxide (through the citric acid cycle) if oxygen supplies are sufficient. When oxygen supplies are insufficient, pyruvate is reduced to lactate. In yeast and other microorganisms, pyruvate is not converted to lactate in the absence of oxygen but instead is converted to ethanol and carbon dioxide.

The amount of ATP formed by the oxidation of glucose depends on whether or not oxygen is present. If oxygen is present, glucose is oxidized to carbon dioxide, and 36–38 ATP molecules are produced for each glucose molecule oxidized, using the combined pathways of glycolysis, the citric acid cycle, the electron transport chain, and oxidative phosphorylation. Thus, approximately 42% of the energy released by the complete oxidation of glucose is conserved by the synthesis of ATP. In the absence of oxygen, only 2 molecules of ATP are formed for each molecule of glucose converted to lactate (2 molecules), and the amount of energy conserved is much less (2%).

Fatty acids, released by the degradation of triglycerides and other lipids, are converted to fatty acyl-CoA, transported into the mitochondria, and oxidized by repeated cycling through a sequence of four reactions known as **β-oxidation**. In each round of β-oxidation, the fatty acyl-CoA is shortened by two carbon atoms as one molecule of acetyl-CoA is formed. The final round of β-oxidation, once the chain has been shortened to four carbon atoms, forms two molecules of acetyl-CoA. β-oxidation also forms the reduced coenzymes $FADH_2$ and NADH, whose reoxidation through the electron transport chain and oxidative phosphorylation leads to the synthesis of ATP. The efficiency of fatty acid oxidation in the human body is approximately 41%.

Amino acids from the breakdown of proteins can be catabolized to provide energy. Amino acids whose carbon skeletons are converted to intermediates that can be converted to glucose through gluconeogenesis are known as **glucogenic amino acids**. Amino acids whose carbon skeletons are broken down to compounds used to form ketone bodies are known as **ketogenic amino acids**.

The first step in amino acid catabolism is separation of the amino group from the carbon skeleton. In a **transamination**, the amino acid gives its NH_2 to pyruvate, α-ketoglutarate, or oxaloacetate. The products of this reaction are a new amino acid and an α-keto acid containing the carbon skeleton of the original amino acid. Pyruvate is transaminated to alanine, α-ketoglutarate to glutamate, and oxaloacetate to aspartate. The amino groups used to form alanine and aspartate are ultimately transferred to α-ketoglutarate, forming glutamate. The glutamate then undergoes **oxidative deamination** to yield α-ketoglutarate and ammonia.

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CHAPTER OVERVIEW

14: Nuclear Chemistry

Most chemists pay little attention to the nucleus of an atom except to consider the number of protons it contains because that determines an element's identity. However, in nuclear chemistry, the composition of the nucleus and the changes that occur there are very important. Applications of nuclear chemistry may be more widespread than you realize. Many people are aware of nuclear power plants and nuclear bombs, but nuclear chemistry also has applications ranging from smoke detectors to medicine, from the sterilization of food to the analysis of ancient artifacts. In this chapter, we will examine some of the basic concepts of nuclear chemistry and some of the nuclear reactions that are important in our everyday lives.

14.0: Prelude to Nuclear Chemistry
14.1: Radioactivity
14.2: Half-Life
14.3: Units of Radioactivity
14.4: Uses of Radioactive Isotopes
14.5: Nuclear Energy
14.E: Nuclear Chemistry (Exercises)
14.S: Nuclear Chemistry (Summary)

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14.0: Prelude to Nuclear Chemistry

Most of us may not be aware of a device in our homes that guards our safety and, at the same time, depends on radioactivity to operate properly. This device is a smoke detector. A typical smoke detector contains an electric circuit that includes two metal plates about 1 cm apart. A battery in the circuit creates a voltage between the plates. Next to the plates is a small disk containing a tiny amount (~0.0002 g) of the radioactive element americium (Am). The radioactivity of the americium ionizes the air between the plates, causing a tiny current to constantly flow between them. (This constant drain on the battery explains why the batteries in smoke detectors should be replaced on a regular basis, whether the alarm has been triggered or not.)



Figure 14.0.1: Many people think of nuclear chemistry in connection with the nuclear power industry and atomic bombs but do not realize that most smoke detectors rely on nuclear chemistry and save countless lives every year. The applications of nuclear chemistry may be more widespread than you think. (CC BY-SA 3.0; Wile e2005).

When particles of smoke from a fire enter the smoke detector, they interfere with the ions between the metal plates, interrupting the tiny flow of current. When the current drops beneath a set value, another circuit triggers a loud alarm, warning of the possible presence of fire. Although radioactive, the americium in a smoke detector is embedded in plastic and is not harmful unless the plastic package is taken apart, which is unlikely. Although many people experience an unfounded fear of radioactivity, smoke detectors provide an application of radioactivity that saves thousands of lives every year.

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14.1: Radioactivity

Learning Objectives

- To define and give examples of the major types of radioactivity.

Atoms are composed of subatomic particles—protons, neutrons, and electrons. Protons and neutrons are located in the nucleus and provide most of the mass of the atom, while electrons circle the nucleus in shells and subshells and account for an atom's size. Remember, the notation for succinctly representing an isotope of a particular atom:

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

The element in this example, represented by the symbol *C*, is carbon. Its atomic number, 6, is the lower left subscript on the symbol and is the number of protons in the atom. The mass number, the superscript to the upper left of the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 12, which means that the number of neutrons in the atom is 12 − 6 = 6 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neutrons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. The two isotopes of hydrogen, ^{2}H and ^{3}H, are given their own names: deuterium (D) and tritium (T), respectively. Another way of expressing a particular isotope is to list the mass number after the element name, like carbon-12 or hydrogen-3.

Atomic theory in the 19th century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source as the atomic nucleus. These emanations were ultimately called, collectively, **radioactivity**.

There are three main forms of radioactive emissions. The first is called an alpha particle, which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use $^{4}_{2}\mathrm{He}$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a chemical equation—for example, the alpha-particle emission of uranium-235 is as follows:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th}$$

How do we know that a product of the reaction is $^{231}_{90}\mathrm{Th}$? We use the law of conservation of matter, which says that matter cannot be created or destroyed. This means we must have the same number of protons and neutrons on both sides of the chemical equation. If our uranium nucleus loses 2 protons, there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose 4 nuclear particles of the original 235, there are 231 remaining. Thus, we use subtraction to identify the isotope of the thorium atom —in this case, $^{231}_{90}\mathrm{Th}$.

Chemists often use the names *parent isotope* and *daughter isotope* to represent the original atom and the product other than the alpha particle. In the previous example, $^{235}_{92}\mathrm{U}$ is the parent isotope, and $^{231}_{90}\mathrm{Th}$ is the daughter isotope. When one element changes into another in this manner, it undergoes *radioactive decay*.

Example 14.1.1

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as $^{222}_{86}\mathrm{Rn}$. We represent the alpha particle as $^{4}_{2}\mathrm{He}$ and use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as an isotope of polonium, $^{218}_{84}\mathrm{Po}$:

$$^{222}_{86}\text{Rn} \rightarrow \ ^{4}_{2}\text{He} + \ ^{218}_{84}\text{Po}$$

Exercise 14.1.1

Write the nuclear equation that represents the radioactive decay of polonium-209 by alpha particle emission and identify the daughter isotope.

Answer

$$^{209}_{84}\text{Po} \rightarrow \ ^{4}_{2}\text{He} + \ ^{205}_{82}\text{Pb}$$

The second major type of radioactive emission is called a beta particle, symbolized by the Greek letter β. A beta particle is an electron ejected from the nucleus (not from the shells of electrons about the nucleus) and has a 1− charge. We can also represent a beta particle as $^{0}_{-1}\text{e}$ or β^{-}. The net effect of beta particle emission on a nucleus is that a neutron is converted to a proton. The overall mass number stays the same, but because the number of protons increases by one, the atomic number goes up by one. Carbon-14 decays by emitting a beta particle:

$$^{14}_{6}\text{C} \ \rightarrow \ ^{14}_{7}\text{N} + \ ^{0}_{-1}\text{e}$$

Again, the sum of the atomic numbers is the same on both sides of the equation, as is the sum of the mass numbers. (Note that the electron is assigned an "atomic number" of 1−, equal to its charge.)

The third major type of radioactive emission is not a particle but rather a very energetic form of electromagnetic radiation called gamma rays, symbolized by the Greek letter γ. Gamma rays themselves do not carry an overall electrical charge, but they may knock electrons out of atoms in a sample of matter and make it electrically charged (for which gamma rays are termed *ionizing radiation*). For example, in the radioactive decay of radon-222, both alpha and gamma radiation are emitted, with the latter having an energy of 8.2×10^{-14} J per nucleus decayed:

$$^{222}_{86}\text{Rn} \rightarrow \ ^{218}_{84}\text{Po} + \ ^{4}_{2}\text{He} + \gamma$$

This may not seem like much energy, but if 1 mol of radon atoms were to decay, the gamma ray energy would be 49 million kJ!

Example 14.1.2

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is $^{12}_{5}\text{B}$ while one of the products is an electron, $^{0}_{-1}\text{e}$. So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus, the complete nuclear equation is as follows:

$$^{12}_{5}\text{B} \rightarrow \ ^{12}_{6}\text{C} + \ ^{0}_{-1}\text{e} + \gamma$$

The daughter isotope is $^{12}_{6}\text{C}$.

Exercise 14.1.2

Write the nuclear equation that represents the radioactive decay of iodine-131 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Answer

$$^{131}_{53}\text{I} \rightarrow \ ^{131}_{54}\text{Xe} + \ ^{0}_{-1}\text{e} + \gamma$$

Alpha, beta, and gamma emissions have different abilities to penetrate matter. The relatively large alpha particle is easily stopped by matter (although it may impart a significant amount of energy to the matter it contacts). Beta particles penetrate slightly into matter, perhaps a few centimeters at most. Gamma rays can penetrate deeply into matter and can impart a large amount of energy into the surrounding matter.

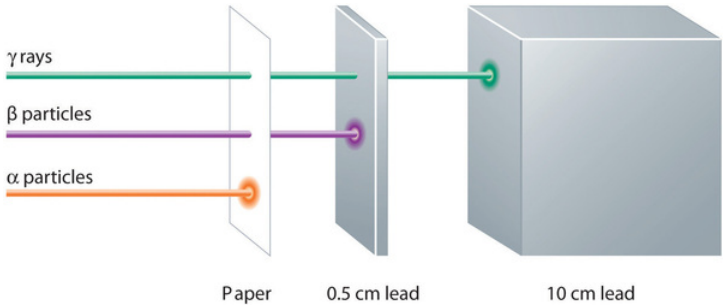


Figure 14.1.2: Different emissions exhibit different penetration powers. (CC BY-NC-SA 3.0; anonymous)

Table 14.1.1 summarizes the properties of the three main types of radioactive emissions.

Table 14.1.1: The Three Main Forms of Radioactive Emissions

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	α, $^{4}_{2}\mathrm{He}$	β, $^{0}_{-1}\mathrm{e}$	γ
identity	helium nucleus	electron	electromagnetic radiation
charge	2+	1−	none
mass number	4	0	0
penetrating power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

Occasionally, an atomic nucleus breaks apart into smaller pieces in a radioactive process called *spontaneous fission* (or fission). Typically, the daughter isotopes produced by fission are a varied mix of products, rather than a specific isotope as with alpha and beta particle emission. Often, fission produces excess neutrons that will sometimes be captured by other nuclei, possibly inducing additional radioactive events. Uranium-235 undergoes spontaneous fission to a small extent. One typical reaction is

$$^{235}_{92}\mathrm{U} \rightarrow {}^{139}_{56}\mathrm{Ba} + {}^{94}_{36}\mathrm{Kr} + 2{}^{1}_{0}\mathrm{n}$$

where $^{1}_{0}\mathrm{n}$ is a neutron. As with any nuclear process, the sums of the atomic numbers and the mass numbers must be the same on both sides of the equation. Spontaneous fission is found only in large nuclei. The smallest nucleus that exhibits spontaneous fission is lead-208.

> *Fission is the radioactive process used in nuclear power plants and one type of nuclear bomb.*

Key Takeaway

The major types of radioactivity include alpha particles, beta particles, and gamma rays.

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14.2: Half-Life

Learning Objectives

- To define *half-life*.
- To determine the amount of radioactive substance remaining after a given number of half-lives.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is the **half-life**. The half-life of a radioactive isotope is the amount of time it takes for one-half of the radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

Consider the following example. Suppose we have 100.0 g of ^{3}H (tritium, a radioactive isotope of hydrogen). It has a half-life of 12.3 y. After 12.3 y, half of the sample will have decayed to ^{3}He by emitting a beta particle, so that only 50.0 g of the original ^{3}H remains. After another 12.3 y—making a total of 24.6 y—another half of the remaining ^{3}H will have decayed, leaving 25.0 g of ^{3}H. After another 12.3 y—now a total of 36.9 y—another half of the remaining ^{3}H will have decayed, leaving 12.5 g of ^{3}H. This sequence of events is illustrated in Figure 14.2.1.

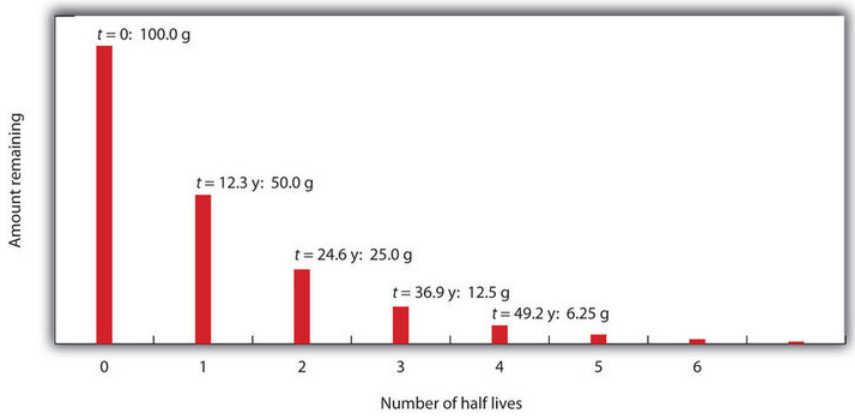


Figure 14.2.1: Radioactive Decay. During each successive half-life, half of the initial amount will radioactively decay.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{n} \tag{14.2.1}$$

where *n* is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 14.2.1

The half-life of ^{20}F is 11.0 s. If a sample initially contains 5.00 g of ^{20}F, how much ^{20}F remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so we can use Equation 14.2.1 with $n = 4$. Substituting and solving results in the following:

$$\begin{aligned}\text{amount remaining} &= 5.00\ g \times \left(\frac{1}{2}\right)^{4} \\ &= 5.00\ g \times \frac{1}{16} \\ &= 0.313\ g\end{aligned}$$

Less than one-third of a gram of ^{20}F remains.

Exercise 14.2.2

The half-life of ^{44}Ti is 60.0 y. A sample initially contains 0.600 g of ^{44}Ti. How much ^{44}Ti remains after 180.0 y?

Answer

0.075 g.

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table 14.2.1 lists the half-lives of some isotopes.

Table 14.2.1: Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5,730 y
^{40}K	1.26×10^{9} y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^{8} y
^{238}U	4.47×10^{9} y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Example 14.2.2

The isotope I-125 is used in certain laboratory procedures and has a half-life of 59.4 days. If the initial activity of a sample of I-125 is $32,000 \text{ counts per minute (cpm)}$, how much activity will be present in 178.2 days?

Solution

We begin by determining how many half-lives are represented by 178.2 days:

$$\frac{178.2 \text{ days}}{59.4 \text{ days/half-life}} = 3 \text{ half-lives}$$

Then we simply count activity:

$$\begin{aligned} \text{initial activity } (t_0) &= 32,000 \text{ cpm} \\ \text{after one half-life} &= 16,000 \text{ cpm} \\ \text{after two half-lives} &= 8,000 \text{ cpm} \\ \text{after three half-lives} &= 4,000 \text{ cpm} \end{aligned}$$

Be sure to keep in mind that the initial count is at time zero (t_0) and we subtract from that count at the first half-life. The second half-life has an activity of half the previous count (not the initial count).

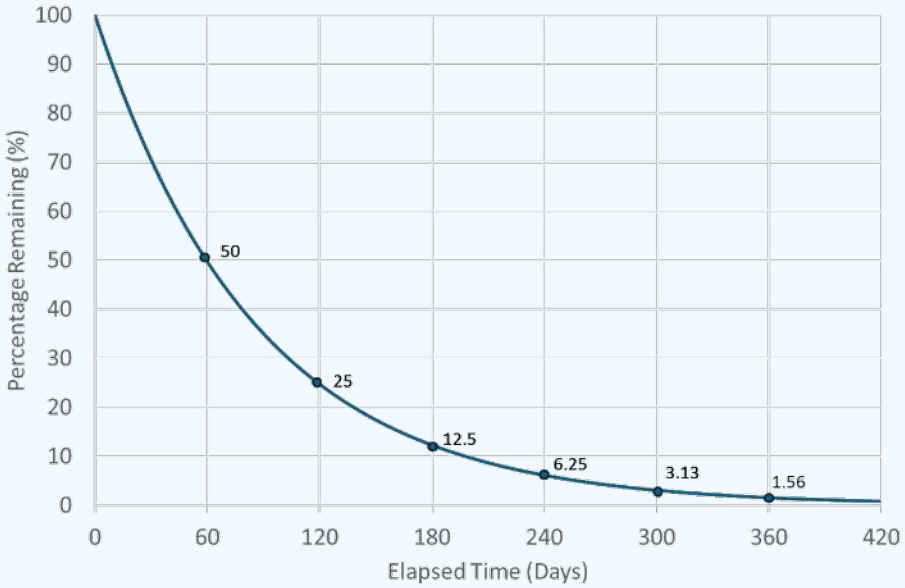
Equation 14.2.1 can be used to calculate the amount of radioactivity remaining after a given time:

$$N_t = N_0 \times (0.5)^{\text{number of half-lives}}$$

where N_t = activity at time t and N_0 = initial activity at time $t = 0$.

If we have an initial activity of $32,000$ cpm, what will the activity be after four half-lives?

$$\begin{aligned} N_t &= N_0\,(0.5)^4 \\ &= (32,000)\,(0.5)\,(0.5)\,(0.5)\,(0.5) \\ &= 2000 \text{ cpm} \end{aligned}$$



Typical radioactive decay curve. (CC BY-NC-SA 3.0; LibreTexts)

The graph above illustrates a typical decay curve for $\mathrm{I}-125$. The activity decreases by one-half during each succeeding half-life.

14.2.2Exercise

A sample of Ac-225 originally contained 80 grams and after 50 days only 2.5 grams of the original Ac-225 remain. What is the half life of Ac-225?

Answer

5 days

Looking Closer: Half-Lives of Radioactive Elements

Many people think that the half-life of a radioactive element represents the amount of time an element is radioactive. In fact, it is the time required for half—not all—of the element to decay radioactively. Occasionally, however, the daughter element is also radioactive, so its radioactivity must also be considered.

The expected working life of an ionization-type smoke detector (described in the opening essay) is about 10 years. In that time, americium-241, which has a half-life of about 432 y, loses less than 4% of its radioactivity. A half-life of 432 y may seem long to us, but it is not very long as half-lives go. Uranium-238, the most common isotope of uranium, has a half-life of about 4.5×10^9 y, while thorium-232 has a half-life of 14×10^9 y.

On the other hand, some nuclei have extremely short half-lives, presenting challenges to the scientists who study them. The longest-lived isotope of lawrencium, ^{262}Lr, has a half-life of 3.6 h, while the shortest-lived isotope of lawrencium, ^{252}Lr, has a half-life of 0.36 s. As of this writing, the largest atom ever detected has atomic number 118, mass number 293, and a half-life of 120 ns. Can you imagine how quickly an experiment must be done to determine the properties of elements that exist for so short a time?

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

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14.3: Units of Radioactivity

Learning Objectives

- To express amounts of radioactivity in a variety of units.

Previously, we used mass to indicate the amount of radioactive substance present. This is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation.

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one becquerel (Bq). Even in a small mass of radioactive material, however, there are many thousands of decays or disintegrations per second. The unit curie (Ci), now defined as 3.7×10^{10} decays per second, was originally defined as the number of decays per second in 1 g of radium. Many radioactive samples have activities that are on the order of microcuries (μCi) or more. Both the becquerel and curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 μCi.

> *The unit becquerel is named after Henri Becquerel, who discovered radioactivity in 1896. The unit curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena and discovered the elements, polonium (Po) and radium (Ra) in the early 1900s.*

Example 14.3.1

A sample of radium has an activity of 16.0 mCi (millicuries). If the half-life of radium is 1,600 y, how long before the sample's activity is 1.0 mCi?

Solution

The following table shows the activity of the radium sample over multiple half-lives:

Solutions to Example 11.3.1

Time in Years	Activity
0	16.0 mCi
1,600	8.0 mCi
3,200	4.0 mCi
4,800	2.0 mCi
6,400	1.0 mCi

Over a period of 4 half-lives, the activity of the radium will be halved four times, at which point its activity will be 1.0 mCi. Thus, it takes 4 half-lives, or 4 × 1,600 y = 6,400 y, for the activity to decrease to 1.0 mCi.

Exercise 14.3.1

A sample of radon has an activity of 60,000 Bq. If the half-life of radon is 15 h, how long before the sample's activity is 3,750 Bq?

Answer

60 hrs.

Other measures of radioactivity are based on the effects it has on living tissue. Radioactivity can transfer energy to tissues in two ways: through the kinetic energy of the particles hitting the tissue and through the electromagnetic energy of the gamma rays being absorbed by the tissue. Either way, the transferred energy—like thermal energy from boiling water—can damage the tissue.

The rad (an acronym for radiation absorbed dose) is a unit equivalent to a gram of tissue absorbing 0.01 J:

$$1 \text{ rad} = 0.01 \text{ J/g}$$

Another unit of radiation absorption is the gray (Gy):

$$1 \text{ Gy} = 100 \text{ rad}$$

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of H_2O (approximately the same mass as a 150 lb person) would increase its temperature by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1×10^{21} molecular C–C bonds in a person's body. That amount of damage would not be desirable.

Predicting the effects of radiation is complicated by the fact that various tissues are affected differently by different types of emissions. To quantify these effects, the unit **rem** (an acronym for roentgen equivalent, man) is defined as

$$\text{rem} = \text{rad} \times \text{RBE}$$

where RBE is the *relative biological effectiveness factor* is a number greater than or equal to 1 that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, RBE factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye tissue, the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X ray is about 20 mrem. A sievert (Sv) is a related unit and is defined as 100 rem.

What is a person's annual exposure to radioactivity and radiation? Table 14.3.1 lists the sources and annual amounts of radiation exposure. It may surprise you to learn that fully 82% of the radioactivity and radiation exposure we receive is from natural sources—sources we cannot avoid. Fully 10% of the exposure comes from our own bodies—largely from ^{14}C and ^{40}K.

Table 14.3.1: Average Annual Radiation Exposure (Approximate)

Source	Amount (mrem)
radon gas	200
medical sources	53
radioactive atoms in the body naturally	39
terrestrial sources	28
cosmic sources	28
consumer products	10
nuclear energy	0.05
Total	358

> *Flying from New York City to San Francisco adds 5 mrem to your overall radiation exposure because the plane flies above much of the atmosphere, which protects us from most cosmic radiation.*

The actual effects of radioactivity and radiation exposure on a person's health depend on the type of radioactivity, the length of exposure, and the tissues exposed. Table 14.3.2 lists the potential threats to health at various amounts of exposure over short periods of time (hours or days).

Table 14.3.2: Effects of Short-Term Exposure to Radioactivity and Radiation

Exposure (rem)	Effect
1 (over a full year)	no detectable effect
~20	increased risk of some cancers
~100	damage to bone marrow and other tissues; possible internal bleeding; decrease in white blood cell count
200–300	visible “burns” on skin, nausea, vomiting, and fatigue
>300	loss of white blood cells; hair loss
~600	death

One of the simplest ways of detecting radioactivity is by using a piece of photographic film embedded in a badge or a pen. On a regular basis, the film is developed and checked for exposure. A comparison of the exposure level of the film with a set of standard exposures indicates the amount of radiation a person was exposed to.



Figure 14.3.1: Detecting Radioactivity. A Geiger counter is a common instrument used to detect radioactivity.

Another means of detecting radioactivity is an electrical device called a Geiger counter (Figure 14.3.1). It contains a gas-filled chamber with a thin membrane on one end that allows radiation emitted from radioactive nuclei to enter the chamber and knock electrons off atoms of gas (usually argon). The presence of electrons and positively charged ions causes a small current, which is detected by the Geiger counter and converted to a signal on a meter or, commonly, an audio circuit to produce an audible “click.”

Key Takeaway

- Radioactivity can be expressed in a variety of units, including rems, rads, and curies.

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14.4: Uses of Radioactive Isotopes

Learning Objectives

- To learn some applications of radioactivity.

Radioactive isotopes have a variety of applications. Generally, however, they are useful either because we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A tracer is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium, ^{3}H, is a radioactive isotope of hydrogen.)

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of radioactive carbon-14 to determine the steps involved in the photosynthesis in plants. We know these steps because researchers followed the progress of the radioactive carbon-14 throughout the process.

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, so the isotope acts like an internal clock. For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about 4.5×10^{9} y. Many analyses like this, using a wide variety of isotopes, have indicated that the age of Earth itself is over 4×10^{9} y. In another interesting example of radioactive dating, ^{3}H dating has been used to verify the stated vintages of some old fine wines.

Carbon-14 (half-life is 5,370 y) is particularly useful in determining the age of once-living artifacts (e.g., animal or plant matter). A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant, although very low, level. Once a living thing dies, however, it no longer acquires carbon-14, and as time passes, the carbon-14 that was in the tissues decays. If a once-living artifact is discovered and analyzed many years after its death, with the remaining carbon-14 compared to the known constant level, an approximate age of the artifact can be determined. Using such methods, scientists determined that the age of the Shroud of Turin (made of linen, which comes from the flax plant, and purported by some to be the burial cloth of Jesus Christ; Figure 14.4.1) is about 600–700 y, not 2,000 y as claimed by some. Scientists were also able to use radiocarbon dating to show that the age of a mummified body found in the ice of the Alps was 5,300 y.

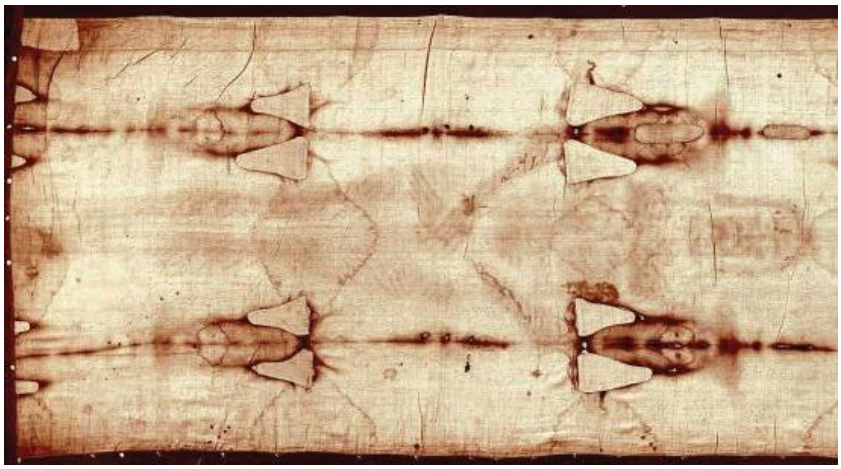


Figure 14.4.1: Shroud of Turin. In 1989, several groups of scientists used carbon-14 dating to demonstrate that the age of the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence. (Public Domain)

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs, which extends the shelf life of these products. Produce such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from coba . This exposure kills a lot of the bacteria that cause spoilage, so the produce stays fresh longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.

Radioactive isotopes have numerous medical applications—diagnosing and treating illnesses and diseases. One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity (Figure 14.4.2). The thyroid gland in the neck is one of the few places in the body with a significant concentration of iodine. To evaluate thyroid activity, a measured dose of iodine-131 is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing trained physicians to diagnose both hyperthyroidism and hypothyroidism. Iodine-131 has a half-life of only 8 d, so the potential for damage due to exposure is minimal. Technetium-99 can also be used to test thyroid function. Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.

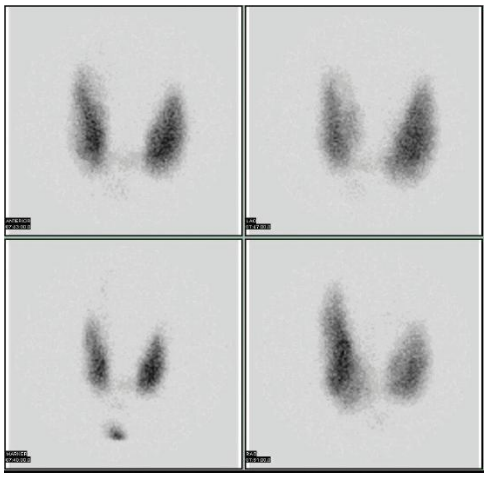


Figure 14.4.2: Medical Diagnostics. Radioactive iodine can be used to image the thyroid gland for diagnostic purposes. (CC BY 3.0 Unported; Myohan via Wikipedia).

Very little radioactive material is needed in these diagnostic techniques because the radiation emitted is so easy to detect. However, therapeutic applications usually require much larger doses because their purpose is to preferentially kill diseased tissues. For example, if a thyroid tumor is detected, a much larger infusion (thousands of rem, as opposed to a diagnostic dose of less then 40 rem) of iodine-131 could help destroy the tumor cells. Similarly, radioactive strontium is used to not only detect but also ease the pain of bone cancers. Table 14.4.1 lists several radioactive isotopes and their medical uses.

Table 14.4.1: Some Radioactive Isotopes That Have Medical Applications

Isotope	Use
^{32}P	cancer detection and treatment, especially in eyes and skin
^{59}Fe	anemia diagnosis
^{60}Co	gamma ray irradiation of tumors
^{99m}Tc	brain, thyroid, liver, bone marrow, lung, heart, and intestinal scanning; blood volume determination
^{131}I	diagnosis and treatment of thyroid function
^{133}Xe	lung imaging
^{198}Au	liver disease diagnosis

In addition to the direct application of radioactive isotopes to diseased tissue, the gamma ray emissions of some isotopes can be directed toward the tissue to be destroyed. Cobalt-60 is a useful isotope for this kind of procedure.

To Your Health: Positron Emission Tomography Scans

One relatively rare form of radioactivity is called *positron emission*. It is similar to beta particle emission, except that instead of emitting an electron, a nucleus emits a positively charged electron, called a *positron*. A positron is actually a piece of antimatter; therefore, when a positron encounters an electron, both particles are converted into high-energy gamma radiation.

Isotopes that emit positrons can be employed in a medical imaging technique called *positron emission tomography* (*PET*). A patient receives a compound containing a positron-emitting isotope, either intravenously or by ingestion. The radioactive compound travels throughout the body, and the patient is then pushed slowly through a ring of sensors that detect the gamma radiation given off by the annihilation of positrons and electrons. A computer connected to the sensors constructs a three-dimensional image of the interior of part or all of the patient's body, allowing doctors to see organs or tumors or regulate the function of various organs (such as the brain or the heart) to diagnose the medical condition of the patient.



Figure 14.4.3: (left) Combined apparatus for positron emission tomography (PET) and X-ray computer tomography (CT), Siemens Biograph. (CC BY-SA 3.0 Unported; Brudersohn via Wikipedia) (right) Whole-body PET scan using 18F-FDG (Public domain; Jens Maus via Wikipedia)

Two isotopes that undergo positron emission are carbon-11 and fluorine-18, with half-lives of 20.4 and 110 min, respectively. Both isotopes can be incorporated into sugar molecules and introduced into the body. Doctors can use the intensity of gamma ray emission to find tissues that metabolize the sugar faster than other tissues; fast-metabolizing tissue is one sign of a malignant (i.e., cancerous) tumor. Researchers use similar techniques to map areas of the brain that are most active during specific tasks, such as reading or speaking.

PET is one of many diagnostic and treatment methods that physicians use to improve the quality of our lives. It is one of the many positive uses of radioactivity in society.

Key Takeaway

- Radioactivity has several practical applications, including tracers, medical applications, dating once-living objects, and the preservation of food.

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14.5: Nuclear Energy

Learning Objectives

- Explain where nuclear energy comes from.
- Describe the difference between fission and fusion.

Nuclear changes occur with a simultaneous release of energy. Where does this energy come from? If we could precisely measure the masses of the reactants and the products of a nuclear reaction, we would notice that the amount of mass drops slightly in the conversion from reactants to products. Consider the following nuclear reaction, in which the molar mass of each species is indicated to four decimal places:

$$\underbrace{^{235}\text{U}}_{235.0439} \rightarrow \underbrace{^{139}\text{Ba}}_{138.9088} + \underbrace{^{94}\text{Kr}}_{93.9343} + \underbrace{2\,^{1}\text{n}}_{2\times1.0087}$$

If we compare the mass of the reactant (235.0439) to the masses of the products (sum = 234.8605), we notice a mass difference of −0.1834 g, or −0.0001834 kg. Where did this mass go?

According to Albert Einstein's theory of relativity, energy (E) and mass (m) are related by the following equation:

$$E = mc^2 \tag{14.5.1}$$

where c is the speed of light, or 3.00 × 10^8 m/s. In the course of the uranium nuclear chemical reaction, the mass difference is converted to energy, which is given off by the reaction:

$$\begin{aligned} E &= (-0.0001834\ kg)(3.00 \times 10^8\ m/s)^2 \\ &= -1.65 \times 10^{13}\ J \\ &= -1.65 \times 10^{10}\ kJ \end{aligned}$$

Hence, 16.5 billion kJ of energy are given off every time 1 mol of uranium-235 undergoes this nuclear reaction. This is an extraordinary amount of energy. Compare it to combustion reactions of hydrocarbons, which give off about 650 kJ/mol of energy for every CH_2 unit in the hydrocarbon—on the order of *hundreds* of kilojoules per mole. Nuclear reactions give off *billions* of kilojoules per mole.

If this energy could be properly harvested, it would be a significant source of energy for our society. Nuclear energy involves the controlled harvesting of energy from fission reactions. The reaction can be controlled because the fission of uranium-235 (and a few other isotopes, such as plutonium-239) can be artificially initiated by injecting a neutron into a uranium nucleus. The overall nuclear equation, with energy included as a product, is then as follows:

$$^{235}\text{U} + {}^{1}\text{n} \longrightarrow {}^{139}\text{Ba} + {}^{94}\text{Kr} + 3\,{}^{1}\text{n} + \text{energy}$$

Thus, by the careful addition of extra neutrons into a sample of uranium, we can control the fission process and obtain energy that can be used for other purposes.

The Curie Family

Artificial or induced radioactivity was first demonstrated in 1934 by Irène Joliot-Curie and Frédéric Joliot, the daughter and son-in-law of Marie Curie.

Example 14.5.1

Plutonium-239 can absorb a neutron and undergo a fission reaction to produce an atom of gold-204 and an atom of phosphorus-31. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

Solution

Using the data given, we can write the following initial equation:

$$^{1}_{0}\text{n} + {}^{239}_{94}\text{Pu} \rightarrow {}^{204}_{79}\text{Au} + {}^{31}_{15}\text{P} + ?{}^{1}_{0}\text{n}$$

In balanced nuclear equations, the sums of the subscripts on each sides of the equation are the same, as are the sums of the superscripts. The subscripts are already balanced: 0 + 94 = 94 and 79 + 15 = 94. The superscripts on the left equal 240 (1 + 239) but equal 235 (204 + 31) on the right. We need five more mass number units on the right. Five neutrons should be the products of the process for the mass numbers to balance. (Because the atomic number of a neutron is zero, including five neutrons on the right does not change the overall sum of the subscripts.) Thus, the balanced nuclear equation is as follows:

$$^{1}_{0}\text{n} + {}^{239}_{94}\text{Pu} \rightarrow {}^{204}_{79}\text{Au} + {}^{31}_{15}\text{P} + 5{}^{1}_{0}\text{n}$$

We predict that the overall process will give off five neutrons.

? Exercise 14.5.1

Uranium-238 can absorb a neutron and undergo a fission reaction to produce an atom of cesium-135 and an atom of rubidium-96. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

Answer

$$^{1}_{0}\text{n} + {}^{238}_{92}\text{U} \rightarrow {}^{135}_{55}\text{Cs} + {}^{96}_{37}\text{Rb} + 8{}^{1}_{0}\text{n}$$

We predict that the overall process will give off eight neutrons.

A nuclear reactor is an apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes. Figure 14.5.1 shows a simplified diagram of a nuclear reactor. The energy from the controlled nuclear reaction converts liquid water into high-pressure steam, which is used to run turbines that generate electricity.

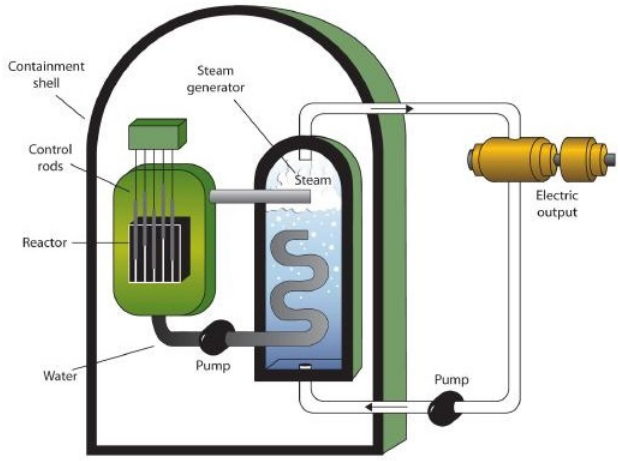


Figure 14.5.1: A Diagram of a Nuclear Power Plant for Generating Electricity. The two main components of the power plant are the nuclear reactor itself and the steam-driven turbine and electricity generator.

Notice that the fission of uranium produces two more free neutrons than were present to begin with. These neutrons can themselves stimulate other uranium nuclei to undergo fission, releasing yet more energy and even more neutrons, which can in turn induce even more uranium fission. A single neutron can thus begin a process that grows exponentially in a phenomenon called a chain reaction:

$$1 \rightarrow 2 \rightarrow 4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow 64 \rightarrow 128 \rightarrow 256 \rightarrow 512 \rightarrow 1{,}024 \rightarrow 2{,}048 \rightarrow 4{,}096 \rightarrow 8{,}192 \rightarrow 16{,}384 \rightarrow \ldots$$

Because energy is produced with each fission event, energy is also produced exponentially and in an uncontrolled fashion. The quick production of energy creates an explosion. This is the mechanism behind the atomic bomb.

The first controlled chain reaction was achieved on December 2, 1942, in an experiment supervised by Enrico Fermi in a laboratory underneath the football stadium at the University of Chicago.

Although fairly simple in theory, an atomic bomb is difficult to produce, in part because uranium-235, the isotope that undergoes fission, makes up only 0.7% of natural uranium; the rest is mostly uranium-238, which does not undergo fission. (Remember that the radioactive process that a nucleus undergoes is characteristic of the isotope.) To make uranium useful for nuclear reactors, the uranium in uranium-235 must be *enriched* to about 3%. Enrichment of uranium is a laborious and costly series of physical and chemical separations. To be useful in an atomic bomb, the uranium in uranium-235 must be enriched to 70% or more. At lesser concentrations, the chain reaction cannot sustain itself, so no explosion is produced.

Fusion is another nuclear process that can be used to produce energy. In this process, smaller nuclei are combined to make larger nuclei, with an accompanying release of energy. One example is the hydrogen fusion, which makes helium. While the steps of the process are complicated, the net reaction is:

$$4\,{}^{1}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + 2.58 \times 10^{12}\ J$$

Notice that the amount of energy given off per mole of reactant is only a fraction of the amount given off by the fission of 1 mol of uranium-235. On a mass (per gram) basis, however, the hydrogen fusion emits many times more energy than fission does. In addition, the product of fission is helium gas, not a wide range of isotopes (some of which are also radioactive) produced by fission.

The practical problem is that to perform fusion, extremely high pressures and temperatures are necessary. Currently, the only known stable systems undergoing fusion are the interiors of stars. The conditions necessary for fusion can be created using an atomic bomb, but the resulting fusion is uncontrollable (and the basis for another type of bomb, a hydrogen bomb). Currently, researchers are looking for safe, controlled ways of producing useful energy using fusion.

Career Focus: Nuclear Medicine Technologist

Generally speaking, a radiological technician deals with X ray equipment and procedures. A *nuclear medicine technologist* has similar responsibilities, using compounds containing radioactive isotopes to help diagnose and treat disease.

Nuclear medicine technologists administer the substances containing the radioactive isotope and subsequently operate the apparatus that detects the radiation produced by radioactive decay. The apparatus may be as simple as a piece of photographic film or as complex as a series of computer-controlled electronic detectors. The images obtained by the technologist are interpreted by a specially trained physician.

One of the chief responsibilities of a nuclear medicine technologist is safety. Improper exposure to radioactivity can be harmful to both patient and technologist alike. Therefore, the technologist must adhere to strict safety standards to keep unnecessary exposure as low as possible. The technologist must also know how to dispose of waste materials safely and appropriately.

Key Takeaways

- Nuclear energy comes from tiny mass changes in nuclei as radioactive processes occur.
- In fission, large nuclei break apart and release energy; in fusion, small nuclei merge together and release energy.

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14.E: Nuclear Chemistry (Exercises)

11.1 Radioactivity

Concept Review Exercise

1. What are the major types of radioactivity? Write chemical equations demonstrating each type.

Answer

1. The major types of radioactivity are alpha decay, beta decay, and gamma ray emission; alpha decay with gamma emission: $^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He} + \gamma$; beta decay: $^{14}_{6}\text{C} \rightarrow {}_{7}{}^{14}\text{N} + {}^{0}_{-1}\text{e}$ (answers will vary)

Exercises

1. Define *radioactivity*.
2. Give an example of a radioactive isotope.
3. How many protons and neutrons are in each isotope?
   a. $^{11}_{5}\text{B}$
   b. $^{27}_{13}\text{Al}$
   c. ^{56}Fe
   d. ^{224}Rn
4. How many protons and neutrons are in each isotope?
   a. $^{2}_{1}\text{H}$
   b. $^{112}_{48}\text{Cd}$
   c. ^{252}Es
   d. ^{40}K
5. Describe an alpha particle. What nucleus is it equivalent to?
6. Describe a beta particle. What subatomic particle is it equivalent to?
7. Explain what gamma rays are.
8. Explain why it is inappropriate to refer to gamma rays as gamma “particles.”
9. Plutonium has an atomic number of 94. Write the chemical equation for the alpha particle emission of ^{244}Pu. What is the daughter isotope?
10. Francium has an atomic number of 87. Write the chemical equation for the alpha particle emission of ^{212}Fr. What is the daughter isotope?
11. Tin has an atomic number of 50. Write the chemical equation for the beta particle emission of ^{121}Sn. What is the daughter isotope?
12. Technetium has an atomic number of 43. Write the chemical equation for the beta particle emission of ^{99}Tc. What is the daughter isotope?
13. Energies of gamma rays are typically expressed in units of megaelectron volts (MeV), where 1 MeV = 1.602×10^{-13} J. Using data provided in the text, calculate the energy, in megaelectron volts, of the gamma ray emitted when radon-222 decays.
14. The gamma ray emitted when oxygen-19 gives off a beta particle is 0.197 MeV. What is its energy in joules? (See Exercise 13 for the definition of a megaelectron volt.)
15. Which penetrates matter more deeply—alpha particles or beta particles? Suggest ways to protect yourself against both particles.
16. Which penetrates matter more deeply—alpha particles or gamma rays? Suggest ways to protect yourself against both emissions.
17. Define *nuclear fission*.

18. What general characteristic is typically necessary for a nucleus to undergo spontaneous fission?

Answers

1. Radioactivity is the spontaneous emission of particles and radiation from atomic nuclei.

2. C-14 or ^{14}C is an example of radioactive isotope (answers may vary).

3.

   a. 5 protons; 6 neutrons
   b. 13 protons; 14 neutrons
   c. 26 protons; 30 neutrons
   d. 86 protons; 138 neutrons

4.

   a. 1 proton; 1 neutron
   b. 48 protons; 64 neutrons
   c. 99 protons;153 neutrons
   d. 19 protons; 21 neutrons

5. An alpha particle is a combination of two protons and two neutrons and is equivalent to a helium nucleus.

6. A beta particle is an electron.

7. Gamma rays are high-energy electromagnetic radiation given off in radioactive decay.

8. Gamma rays have no mass. Hence not a particle.

9. $^{244}_{94}\text{Pu} \rightarrow {}^{4}_{2}\text{He} + {}^{240}_{92}\text{U}$; the daughter isotope is $^{240}_{92}\text{U}$, an atom of uranium.

10. $^{212}_{87}\text{Fr} \rightarrow {}^{4}_{2}\text{He} + {}^{208}_{85}\text{At}$; the daughter isotope is $^{208}_{85}\text{At}$, an atom of astatine.

11. $^{121}_{50}\text{Sn} \rightarrow {}^{0}_{-1}\text{e} + {}^{121}_{51}\text{Sb}$; the daughter isotope is $^{121}_{51}\text{Sb}$, an atom of antimony.

12. $^{99}_{43}\text{Tc} \rightarrow {}^{0}_{-1}\text{e} + {}^{99}_{44}\text{Mo}$; the daughter isotope is $^{99}_{44}\text{Mo}$, an atom of antimony.

13. 0.512 MeV

14. 3.16×10^{-14} J

15. Beta particles; shielding of the appropriate thickness can protect against both alpha and beta particles.

16. Gamma rays; can be shielded by thick, dense material such as lead (Pb). Alpha particles has low energy; can shielded by a piece of paper.

17. Nuclear fission is when large nuclei break down into smaller nuclei.

18. A nucleus must be very large. Examples are Th-232 and U-235.

11.2 Half-Life

Concept Review Exercises

1. Define *half-life*.
2. Describe a way to determine the amount of radioactive isotope remaining after a given number of half-lives.

Answers

1. Half-life is the amount of time needed for half of a radioactive material to decay.
2. take half of the initial amount for each half-life of time elapsed

Exercises

1. Do all isotopes have a half-life? Explain.

2. Which is more radioactive—an isotope with a long half-life or an isotope with a short half-life?

3. What percent of a sample remains after one half-life? Three half-lives?

4. The half-life of polonium-218 is 3.0 min. How much of a 0.540 mg sample would remain after 9.0 minutes have passed?

5. The half-life of protactinium-234 is 6.69 hours. If a 0.812 mg sample of Pa-239 decays for 40.14 hours, what mass of the isotope remains?

6. How long does it take for 1.00 g of ^{103}Pd to decay to 0.125 g if its half-life is 17.0 d?

7. How long does it take for 2.00 g of ^{94}Nb to decay to 0.0625 g if its half-life is 20,000 y?

8. It took 75 y for 10.0 g of a radioactive isotope to decay to 1.25 g. What is the half-life of this isotope?

9. It took 49.2 s for 3.000 g of a radioactive isotope to decay to 0.1875 g. What is the half-life of this isotope?

Answers

1. Only radioactive isotopes have half-lives.

2. An isotope with a shorter half-life decay more rapidly is more radioactive.

3. 1 half-life: 50%; 3 half-lives: 12.5%

4. 9.0 min = 3 half-lives (make 3 arrows): 0.540 mg --> 0.270 mg --> 0.135 mg --> 0.0675 mg

5. 0.0127 mg

6. 51.0 d

7. 100 000 y

8. 25 y

9. 12.3 s

11.3 Units of Radioactivity

Concept Review Exercise

1. What units are used to quantify radioactivity?

Answer

1. the curie, the becquerel, the rad, the gray, the sievert, and the rem

Exercises

1. Define *rad*.

2. Define *rem*.

3. How does a becquerel differ from a curie?

4. How is the curie defined?

5. A sample of radon gas has an activity of 140.0 mCi. If the half-life of radon is 1,500 y, how long before the activity of the sample is 8.75 mCi?

6. A sample of curium has an activity of 1,600 Bq. If the half-life of curium is 24.0 s, how long before its activity is 25.0 Bq?

7. If a radioactive sample has an activity of 65 µCi, how many disintegrations per second are occurring?

8. If a radioactive sample has an activity of 7.55×10^5 Bq, how many disintegrations per second are occurring?

9. Describe how a radiation exposure in rems is determined.

10. Which contributes more to the rems of exposure—alpha or beta particles? Why?

11. Use Table 11.3.2 to determine which sources of radiation exposure are inescapable and which can be avoided. What percentage of radiation is unavoidable?

12. What percentage of the approximate annual radiation exposure comes from radioactive atoms that are in the body naturally?

13. Explain how a film badge works to detect radiation.

14. Explain how a Geiger counter works to detect radiation.

Answers

1. Known as the radiation absorbed dose, a rad is the absorption of 0.01 J/g of tissue.

2. Known as roentgen equivalent man, a rem is an absorption of one rad times a factor. The factor is variable depending on the type of emission and the type of irradiated tissue.

3. A becquerel is smaller and equals 1 decay per second. A curie is 3.7×10^{10} Bq.

4. A curie is defined as 3.7×10^{10} decays per second.

5. 6000 y

6. 144 s

7. 2.41×10^{6} disintegrations per second

8. 7.55×10^{5} disintegrations per second

9. The radiation exposure is determined by the number of rads times the quality factor of the radiation.

10. Alpha contributes more than beta because of its bigger size and electrical charge.

11. At least 16% (terrestrial and cosmic sources) of radioactivity is unavoidable; the rest depends on what else a person is exposed to.

12. About 11% come from radioactive atoms that are in the body naturally.

13. A film badge uses film, which is exposed as it is subjected to radiation.

14. The Geiger counter consists of a tube with electrodes and is filled with an inert (argon) gas. Radiation entering the tube ionizes the gas, and the ions are attracted to the electrodes and produce an electric pulse (clicking sound).

11.4 Uses of Radioactive Isotopes

Concept Review Exercise

1. Describe some of the different ways that amounts of radioactivity are applied in society.

Answer

1. Radioactive isotopes are used in dating, as tracers, and in medicine as diagnostic and treatment tools.

Exercises

1. Define *tracer* is and give an example of how tracers work.

2. Name two isotopes that have been used as tracers.

3. Explain how radioactive dating works.

4. Name an isotope that has been used in radioactive dating.

5. The current disintegration rate for carbon-14 is 14.0 Bq. A sample of burnt wood discovered in an archaeological excavation is found to have a carbon-14 decay rate of 3.5 Bq. If the half-life of carbon-14 is 5,700 y, approximately how old is the wood sample?

6. A small asteroid crashes to Earth. After chemical analysis, it is found to contain 1 g of technetium-99 to every 3 g of ruthenium-99, its daughter isotope. If the half-life of technetium-99 is 210,000 y, approximately how old is the asteroid?

7. What do you think are some of the positive aspects of irradiation of food?

8. What do you think are some of the negative aspects of irradiation of food?

9. Describe how iodine-131 is used to both diagnose and treat thyroid problems.

10. List at least five organs that can be imaged using radioactive isotopes.

11. Which radioactive emissions can be used therapeutically?

12. Which isotope is used in therapeutics primarily for its gamma ray emissions?

13. What volume of a radioisotope should be given if a patient needs 125 mCi of a solution which contains 45 mCi in 5.0 mL?

14. Sodium-24 is used to treat leukemia. A 36-kg patient is prescribed 145 μCi/kg and it is supplied to the hospital in a vial containing 250 μCi/mL. What volume should be given to the patient?

15. Lead-212 is one of the radioisotopes used in the treatment of breast cancer. A patient needs a 15 μCi dose and it is supplied as a solution with a concentration of 2.5 μCi/mL. What volume does the patient need? Given the half-life of lead is 10.6 hours, what will be the radioactivity of the sample after approximately four days?

Answers

1. A tracer follows the path of a chemical or a physical process. One of the uses of a tracer is following the path of water underground (answers will vary).

2. Tritium (^{3}H) and Carbon-14 (^{14}C) (answers will vary)

3. Radioactive dating works by comparing the amounts of parent and daughter isotopes and calculating back to how long ago all of the material was just the parent isotope.

4. Carbon-14 (^{14}C) and Uranium-235 (^{235}U) (answers will vary)

5. about 11,400 y

6. about 420,000 y

7. increased shelf life (answers will vary)

8. reduction in the food's vitamin content and cost

9. Iodine-131 is preferentially absorbed by the thyroid gland and can be used to measure the gland’s activity or destroy bad cells in the gland.

10. brain, bone, heart, thyroid, lung (answers will vary)

11. gamma rays, beta particles, or alpha particles

12. cobalt-60

13. 125mCi x (5.0mL/45mCi)=14mL

14. 36kg x (145μCi/kg) x (1mL/250μCi)=21mL

15. Volume given: 15μCi x (1mL/2.5μCi) = 6.0mL

Elapsed time in hours: 4 days x (24 hr/day) = 96 hr

Number of half-lives: 96 hrs/10.6 hours = 9

Radioactivity remaining after 9 half-lives: 0.029 μCi

11.5 Nuclear Energy

Concept Review Exercises

1. How is nuclear energy produced?

2. What is the difference between fission and fusion?

Answers

1. Nuclear energy is produced by carefully controlling the speed of a fission reaction.

2. In fission, large nuclei break down into small ones; in fusion, small nuclei combine to make larger ones. In both cases, a lot of energy is emitted.

Exercises

1. In the spontaneous fission of uranium-233, the following reaction occurs:

   $^{233}U + {}^{1}n \rightarrow {}^{142}Ce + {}^{82}Se + 10{}^{1}n$

   For every mole of ^{233}U that decays, 0.1355 g of mass is lost. How much energy is given off per mole of ^{233}U reacted?

2. In the spontaneous fission of plutonium-241, the following reaction occurs:

   $^{241}Pu + {}^{1}n \rightarrow {}^{104}Ru + {}^{124}Sn + 14{}^{1}n$

   For every mole of ^{241}Pu that decays, 0.1326 g of mass is lost. How much energy is given off per mole of ^{241}Pu reacted?

3. The two rarer isotopes of hydrogen—deuterium and tritium—can also be fused to make helium by the following reaction:

   $^{2}H + {}^{3}H \rightarrow {}^{4}He + {}^{1}n$

   In the course of this reaction, 0.01888 g of mass is lost. How much energy is emitted in the reaction of 1 mol of deuterium and tritium?

4. A process called *helium burning* is thought to occur inside older stars, forming carbon:

   $3{}^{4}He \rightarrow {}^{12}C$

   If the reaction proceeds with 0.00781 g of mass lost on a molar basis, how much energy is given off?

5. Briefly describe how a nuclear reactor generates electricity.

6. Briefly describe the difference between how a nuclear reactor works and how a nuclear bomb works.

7. What is a chain reaction?

8. Why must uranium be enriched to supply nuclear energy?

Answers

1. 1.22×10^{13} J

2. 1.19×10^{13} J

3. 1.70×10^{12} J

4. 7.03×10^{11} J

5. A nuclear reactor generates heat, which is used to generate steam that turns a turbine to generate electricity.

6. Both nuclear reactor and nuclear bomb are powered by fission reaction however, in a nuclear reactor, the fission is monitored and controlled to occur continuously for a much longer time. In a nuclear bomb, the reaction is uncontrolled to explode in one event.

7. A chain reaction is an ever-expanding series of processes that, if left unchecked, can cause a runaway reaction and possibly an explosion.

8. Natural uranium ores contain only 0.7% U-235. Most nuclear reactors require enriched U-235 for their fuel.

11.6: Chapter Summary

Additional Exercises

1. Given that many elements are metals, suggest why it would be unsafe to have radioactive materials in contact with acids.

2. Many alpha-emitting radioactive substances are relatively safe to handle, but inhaling radioactive dust can be very dangerous. Why?

3. Uranium can be separated from its daughter isotope thorium by dissolving a sample in acid and adding sodium iodide, which precipitates thorium(III) iodide:

   $Th^{3+}(aq) + 3I^{-}(aq) \rightarrow ThI_3(s)$

   If 0.567 g of Th^{3+} were dissolved in solution, how many milliliters of 0.500 M NaI(aq) would have to be added to precipitate all the thorium?

4. Thorium oxide can be dissolved in an acidic solution:

   $ThO_2(s) + 4H^{+} \rightarrow Th^{4+}(aq) + 2H_2O(\ell)$

   How many milliliters of 1.55 M HCl(aq) are needed to dissolve 10.65 g of ThO_2?

5. Radioactive strontium is dangerous because it can chemically replace calcium in the human body. The bones are particularly susceptible to radiation damage. Write the nuclear equation for the beta emission of strontium-90.

6. Write the nuclear equation for the beta emission of iodine-131, the isotope used to diagnose and treat thyroid problems.

7. A common uranium compound is uranyl nitrate hexahydrate [$UO_2(NO_3)_2$_$6H_2O$]. What is the formula mass of this compound?

8. Plutonium forms three oxides: PuO, PuO_2, and Pu_2O_3. What are the formula masses of these three compounds?

9. A banana contains 600 mg of potassium, 0.0117% of which is radioactive potassium-40. If 1 g of potassium-40 has an activity of 2.626×10^5 Bq, what is the activity of a banana?

10. Smoke detectors typically contain about 0.25 mg of americium-241 as part of the smoke detection mechanism. If the activity of 1 g of americium-241 is 1.26×10^{11} Bq, what is the activity of americium-241 in the smoke detector?

11. Uranium hexafluoride (UF_6) reacts with water to make uranyl fluoride (UO_2F_2) and hydrogen fluoride (HF). Balance the following chemical equation:

    $UF_6 + H_2O \rightarrow UO_2F_2 + HF$

12. The cyclopentadienyl anion ($C_5H_5^{-}$) is an organic ion that can make ionic compounds with positive ions of radioactive elements, such as Np^{3+}. Balance the following chemical equation:

    $NpCl_3 + Be(C_5H_5)_2 \rightarrow Np(C_5H_5)_3 + BeCl_2$

Answers

1. Acids can dissolve metals, making aqueous solutions.

2. Alpha rays are dangerous only when the alpha emitter is in direct contact with tissue cells inside the body.

3. 14.7 mL

4. 104 mL

5. $^{90}_{38}\text{Sr} \rightarrow {}^{0}_{-1}\text{e} + {}^{90}_{39}\text{Y}$

6. $^{131}_{53}\text{I} \rightarrow {}^{0}_{-1}\text{e} + {}^{131}_{54}\text{Xe}$

7. 502 g/mol

8. PuO = 260.06 g/mol; PuO_2 = 276.06 g/mol; Pu_2O_3 = 536.12 g/mol

9. about 18 Bq

10. 3.15 x 10^7 Bq

11. $UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$

12. $2NpCl_3 + 3Be(C_5H_5)_2 \rightarrow 2Np(C_5H_5)_3 + 3BeCl_2$

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14.S: Nuclear Chemistry (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.

Some atoms have unstable nuclei that emit particles and high-energy electromagnetic radiation to form new elements that are more stable. This emission of particles and electromagnetic radiation is called **radioactivity**. There are three main types of spontaneous radioactive emission: **alpha particles**, which are equivalent to helium nuclei; **beta particles**, which are electrons; and **gamma radiation**, which is high-energy electromagnetic radiation. Another type of radioactive process is **spontaneous fission**, in which large nuclei spontaneously break apart into smaller nuclei and, often, neutrons. In all forms of radioactivity, new elements are formed from the radioactive reactants.

Radioactive isotopes decay at different rates. The rate of an isotope's decay is expressed as a **half-life**, which is the amount of time required for half of the original material to decay. The length of its half-life is a characteristic of the particular isotope and can range from less than microseconds to billions of years.

Amounts of radioactivity are measured in several different ways. A **becquerel** is equal to one radioactive decay per second. A **curie** represents 3.7×10^{10} decays per second. Other units describe the amount of energy absorbed by body tissues. One **rad** is equivalent to 0.01 joule of energy absorbed per gram of tissue. Different tissues react differently to different types of radioactivity. The **rem** unit takes into account not only the energy absorbed by the tissues, but also includes a numerical multiplication factor to account for the type of radioactivity and the type of tissue. The average annual radiation exposure of a person is less than 360 millirem, over 80% of which is from natural sources. Radioactivity can be detected using photographic film or other devices such as **Geiger counters**.

Radioactive isotopes have many useful applications. They can be used as **tracers** to follow the journey of a substance through a system, like an underground waterway or a metabolic pathway. Radioactive isotopes can be used to date objects, since the amount of parent and daughter isotopes can sometimes be measured very accurately. Radioactive emission can be used to sterilize food for a longer edible lifetime. There are also a number of diagnostic and therapeutic medical applications for radioactive isotopes.

Radioactive processes occur with simultaneous changes in energy. This **nuclear energy** can be used to generate power for human use. **Nuclear reactors** use the energy released by fission of large isotopes to generate electricity. When carefully controlled, fission can produce a **chain reaction** that facilitates the continuous production of energy. If not carefully controlled, a very quick production of energy can result, as in an **atomic bomb**. Natural uranium does not contain enough of the proper isotope of uranium to work in a nuclear reactor, so it must first be **enriched** in uranium-235. Forcing small nuclei together to make larger nuclei, a process called **fusion**, also gives off energy; however, scientists have yet to achieve a controlled fusion process.

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